

TABLES OF PROPERTIES OF GASES

WITH DISSOCIATION THEORY
AND ITS APPLICATIONS

BY

E. W. GEYER, B.Sc., Ph.D.

SENIOR LECTURER IN THE THEORY AND PRACTICE OF HEAT ENGINES,
UNIVERSITY OF GLASGOW

AND

E. A. BRUGES, B.Sc.

ASSISTANT LECTURER IN THE THEORY AND PRACTICE OF HEAT ENGINES,
UNIVERSITY OF GLASGOW

CHECKED

With diagrams

LONGMANS, GREEN AND CO.
LONDON + NEW YORK + TORONTO

LONGMANS, GREEN AND CO. LTD.

6 & 7 CLIFFORD STREET, LONDON W.1

NICOL ROAD, BOMBAY 1

17 CHITTARANJAN AVENUE, CALCUTTA 13

36A MOUNT ROAD, MADRAS 2

55 FIFTH AVENUE, NEW YORK 3

LONGMANS, GREEN AND CO. INC.

LONGMANS, GREEN AND CO.

215 VICTORIA STREET, TORONTO 1

CODE NUMBER 86418

PRINTED IN GREAT BRITAIN BY ROBERT MACLEHOSE AND
THE UNIVERSITY PRESS, GLASGOW

PREFACE

THE thermal properties of gases are used so extensively in engineering design that we feel justified in the publication of the present set of tables, which are based on the results of modern statistical thermodynamic analyses carried out by the various authorities to whom reference is made later. We agree with Heck ⁽¹⁾* when he states that it is preferable to use tables of the properties of gases against temperature rather than equations which show the relationship between the properties and temperature. The tables have accordingly been arranged to run from 400° F. abs. to 5400° F. abs., or, in a few cases to higher temperatures, by 100° F. intervals. Differences in the thermal properties are also printed so that by linear interpolation it is possible to evaluate these properties for any intermediate temperature. In practice this will be found considerably more convenient than the commonly adopted method of making use of equations for specific heats. In any case the latest specific heats cannot conveniently be expressed by any simple equation covering more than a limited range of temperature. In an article published by one of us in *Engineering*, ⁽²⁾ tables of thermal properties have already appeared but, as explained later, the properties presented in this volume have been built up from absolute zero temperature by regarding the gases as being in the hypothetical gaseous state throughout. This is of considerable assistance in dealing with problems on thermal equilibrium and enables the absolute entropy of a gas or mixture of gases to be calculated.

We trust that our explanation of the derivation of the tables and also of the modern approach to the theory of dissociation may prove of interest to engineers who have to deal with combustion problems. A valuable contribution on dissociation as affecting the engineer was made by Goodenough, ⁽³⁾ but at that time the accepted specific heats were inaccurate and in addition the simple evaluation of equilibrium constants by the free energy method had not yet been developed. We feel that this method should be more widely known by engineers and have, therefore, devoted space to its description and application.

We have much pleasure in acknowledging our indebtedness to Professor James Small for his helpful encouragement and criticisms. Our thanks are due also to the authorities of the University of Glasgow for the opportunities extended to us of doing this work and for the facilities we were privileged to use in connection with it.

E. W. GEYER.

E. A. BRUGES.

* References are to the bibliography, for which see p. 70.

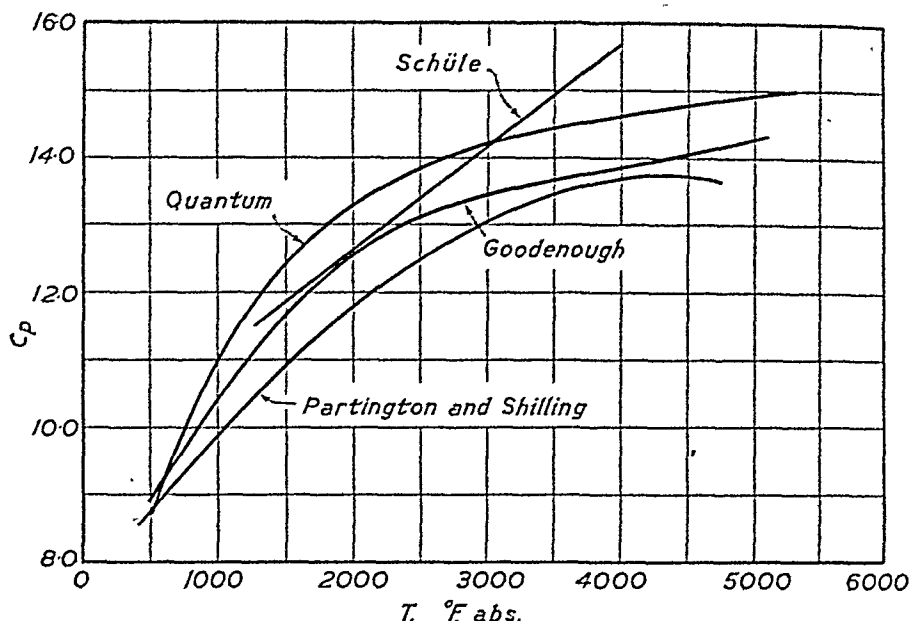
CONTENTS

	PAGE
PREFACE	
PRINCIPLES UPON WHICH THE TABLES ARE BASED	
1. INTRODUCTION - - - - -	7
2. MOLAL MAGNITUDES - - - - -	7
3. ENTROPY - - - - -	9
4. TOTAL HEAT - - - - -	18
5. INTERNAL ENERGY - - - - -	20
6. LOWER HEATS OF REACTION - - - - -	20
7. MAXIMUM WORK OF REACTION AND EQUILIBRIUM CONSTANT - - - - -	23
8. FREE ENERGY - - - - -	25
EXAMPLES ON USE OF TABLES - - - - -	28-70
BIBLIOGRAPHY - - - - -	70
SYMBOLS USED IN TABLES. REFERENCES TO PROPERTIES -	71
TABLES - - - - -	72-102

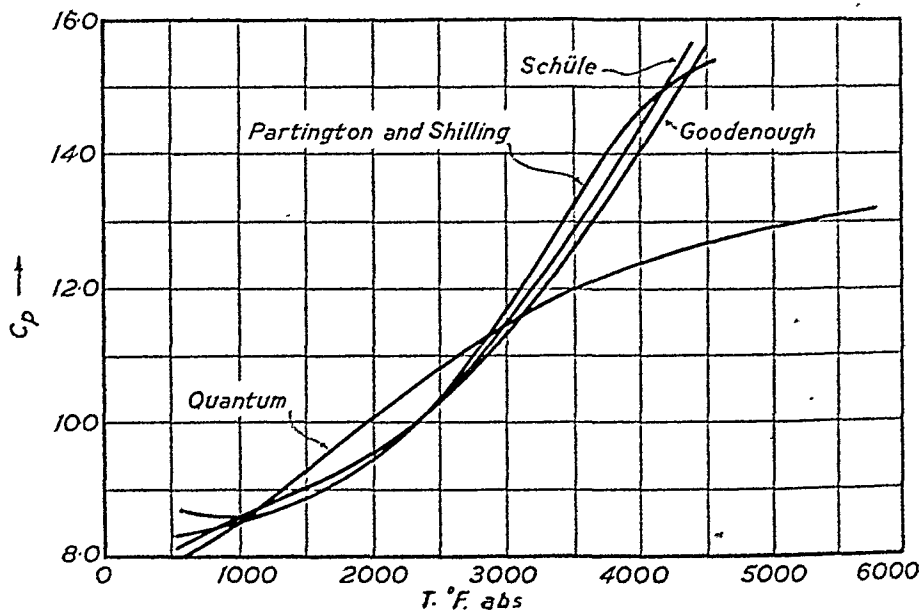
PRINCIPLES UPON WHICH THE TABLES ARE BASED

1. Introduction. The thermal properties of gases, which are presented in this volume, are based on the latest quantum specific heat values calculated by various physicists who have also checked them by spectroscopic analysis. The tables are applicable to the solution of ordinary engineering thermodynamic problems, some of which are given as examples later. In addition, however, they enable an accurate analysis of technical combustion processes, including dissociation effects, to be made. When the mixture of the products of combustion, found in the exhaust pipe of an internal combustion engine or in the flues of a steam boiler, is analysed, it is found generally to consist of the four gases CO_2 , H_2O , O_2 and N_2 . It has long been known, however, that a change in the physical condition of the mixture, such as an increase in temperature or decrease in pressure, tends to cause a splitting up of part of the CO_2 to CO and O_2 and of part of the H_2O to H_2 and O_2 . Other changes may also occur such as the formation of OH and NO . These effects are known as dissociation, a name coined by Sainte-Clair Deville,⁽⁴⁾ who spent the greater part of his life in its study. Later work was carried out by Gibbs,⁽⁵⁾ Horstmann,⁽⁶⁾ Haber,⁽⁷⁾ Nernst⁽⁸⁾ and van't Hoff.⁽⁹⁾ This early work was not generally regarded as of importance to engineers until such authorities as Clerk,⁽¹⁰⁾ Tizard and Pye,⁽¹¹⁾ Goodenough⁽¹²⁾ and Schüle⁽¹³⁾ had drawn attention to the effects of dissociation on technical combustion processes. For comparative purposes, modern values of specific heats, along with those suggested by various authorities two or three decades ago, for the technically important gases CO_2 , H_2O , O_2 and N_2 have been plotted to a base of temperature in ° F. abs. in figs. 1, 2 and 3. It will be observed that the differences between the modern quantum values and the older ones are considerable, so that the errors in calculations involving the old specific heats may be large, and justify the publication of new thermal data and their application to combustion problems including dissociation. Since the work is intended for the use of engineers the thermal data are given in the form of tables in which the temperatures range from 400° F. abs. to 5400° F. abs. (in some cases to 9000° F. abs.) by 100° F. intervals.

2. Molal Magnitudes. It is convenient to express thermal magnitudes, of which internal energy and total heat are examples, in terms of the pound molecule or mol. The unit of mass is thus taken as m lb. where m is the molecular weight of a single gas or the apparent

FIG. 1. Molecular specific heats of CO_2 .

molecular weight of a mixture of gases. If the engineer desires to express any of these magnitudes per pound he has merely to divide them by the molecular weight when dealing with a single gas or by the apparent molecular weight when dealing with a mixture of gases. They are given at 100°F. temperature intervals and intermediate values are obtained by linear interpolation of the differences, which are also

FIG. 2. Molecular specific heats of H_2O .

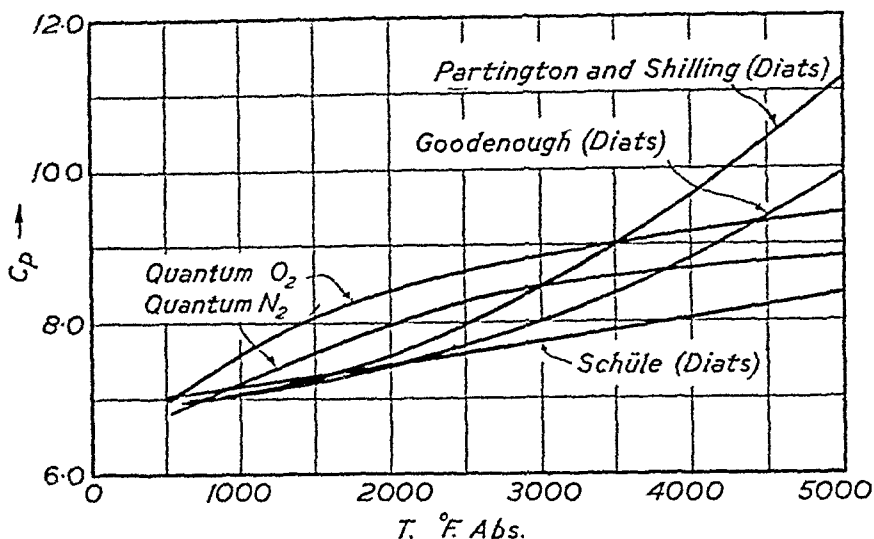


FIG. 3. Molecular specific heats of diatomics.

tabulated. The magnitudes and symbols listed in the tables are entropy, S ; internal energy, E ; total heat, H ; lower heats of reaction at constant volume, H_v and constant pressure, H_p ; equilibrium constant, K_p and a function of free energy expressed by $-\frac{F}{T}$. (See p. 25.)

3. Entropy. The entropy values are absolute, that is, they are all reckoned from absolute zero temperature. This has been rendered possible by the Nernst heat theorem,⁽¹⁴⁾ which states that the entropy of all crystalline solids at absolute zero temperature is zero and that at very low temperatures, say, within 10 to 20° C. abs., the entropy values are small and, as the temperature is lowered to zero, they approach zero asymptotically. Since it is possible to measure specific heats of these crystalline solids between 10 and 20° C. abs. and since the Nernst heat theorem shows that extrapolation to absolute zero temperature is permissible, the absolute entropy values are calculable. Fig. 4 represents the entropy change of 1 gm. mol of oxygen when heated at a pressure of one atmosphere from zero absolute temperature to 298.1° C. abs. (25° C.). As shown by Debye,⁽¹⁵⁾ the specific heat of crystalline solids at temperatures below 15° C. abs. is given by $C_p = kT^3$ and hence the entropy is given by

$$S = \int_0^T \frac{C_p dT}{T} = \int_0^T kT^2 dT = \frac{1}{3} kT^3 \text{ or } \frac{1}{3} C_p.$$

It is thus possible to write down the entropy value when C_p is determined. For solid oxygen, $C_p = 0.963$ at $T = 11.75^\circ$ C. abs. as given by

Johnson and Walker,⁽¹⁵⁾ so that $S=0.321$ E.U. (Entropy Unit), and $k=5.95 \times 10^{-4}$. Between 0° C. abs. and 11.75° C. abs. the entropy values, as given by $\frac{1}{3}kT^3$, are as follows :

T	1	2	3	4
S	1.98×10^{-4}	1.58×10^{-3}	5.35×10^{-3}	1.27×10^{-2}
T	5	6	7	8
S	2.47×10^{-2}	4.28×10^{-2}	6.78×10^{-2}	1.012×10^{-1}
T	9	10	11.75	
S	1.444×10^{-1}	1.98×10^{-1}	3.21×10^{-1}	

The experimentally determined values of C_p between 12.97° C. abs. and 23.66° C. abs. enable the entropy values to be found by graphical integration. Thus, since the increment of entropy, as the temperature is increased from T to $T + \Delta T$, is given by

$$S = \int_T^{T+\Delta T} \frac{C_p dT}{T},$$

it is only necessary to plot values of $\frac{C_p}{T}$ to a base of temperature and

integrate the area below the curve thus found to give the corresponding entropy increments. The total increment of entropy between 11.75° C. abs. and 23.66° C. abs., found in this way, is 1.697 E.U., and hence the entropy increase from A to B is $0.321 + 1.697 = 2.018$ E.U. At 23.66° C. abs., as shown by BC in fig. 4, the first transition in the solid state occurs, the heat involved being 22.42 cal./gm. mol. The accompanying entropy increase is $\frac{22.42}{23.66} = 0.948$ E.U. At 43.76° C. abs. a second

transition occurs (DE) and the increase in entropy between the two points C and D is again found graphically and amounts to 4.661 E.U. At this second transition point the heat of transition is 177.6 cal./gm.

mol. giving $\frac{177.6}{43.76} = 4.058$ E.U. $= DE$ as the entropy increase. Between

43.76° C. abs. and 54.39° C. abs., i.e. between E and F the C_p values give the increase in entropy as 2.397 E.U. Up to 54.39° C. abs. the oxygen has remained in the solid state and at 54.39° C. abs. melting occurs, as shown by the line FG , the latent heat of fusion being 106.3 cal./gm. mol. so that the entropy increase is $\frac{106.3}{54.39} = 1.954$ E.U.

Between 54.39° C. abs. and 90.13° C. abs., i.e. between G and H the oxygen remains in the liquid state and from the given C_p values the increase in the entropy is again found graphically and amounts to 6.462 E.U. Boiling occurs (HJ) at 90.13° C. abs., the latent heat being 1628.8 cal./gm. mol, so that the corresponding entropy increase is

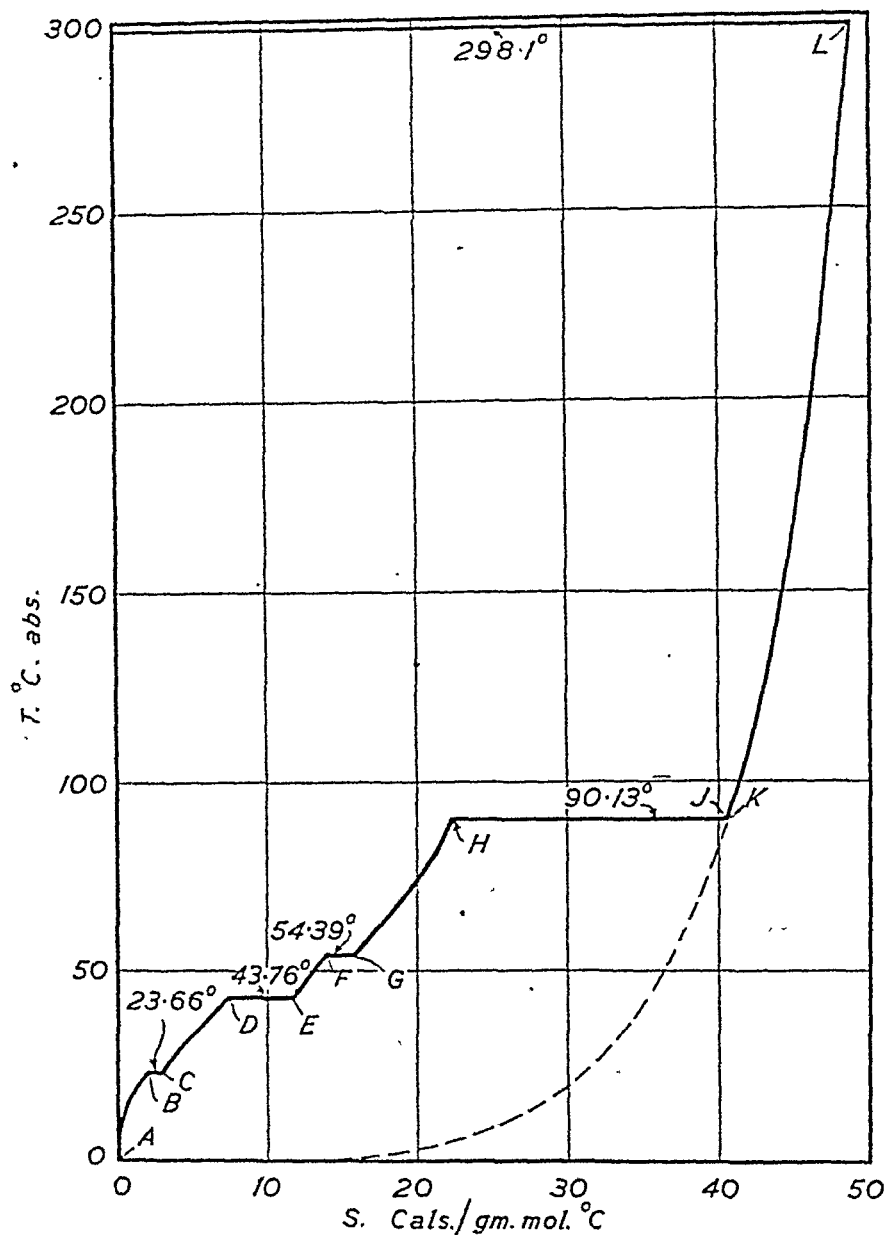


FIG. 4.

$\frac{1628.8}{90.13} = 18.07 \text{ E.U.}$ The sum of the entropies taken over all the phases up to the point J amounts to 40.57 E.U. In order to bring the oxygen to what is called the standard state, which is necessary if the entropy is to be compared with spectroscopic data, the physicists apply a correction amounting to $\frac{27T_c^3P}{32T^3P_c}$, where T_c and P_c are the critical temperature

and critical pressure. This correction moves the state point from J to K but the scale of the diagram is such that the gap between the points does not show. The correction is deduced as follows. On the TS diagram (fig. 5) let J represent the state point of the actual gas at pressure p and temperature T , and K that of oxygen assumed to be reduced to the condition of a perfect gas having the characteristic equation $PV=RT$. If the pressure of both the actual and hypothetical gases is reduced, their state points approach one another until, in the limit when the pressure is zero, they actually coincide. This condition

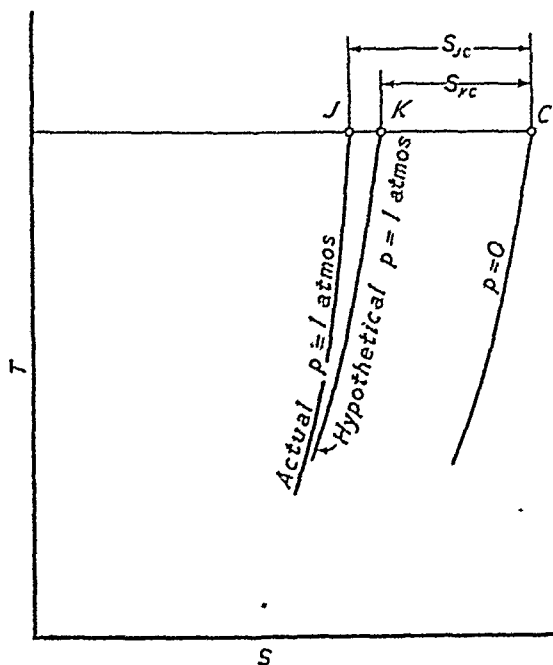


FIG. 5.

is represented by the point C , which is at infinite distance from J and K , but we are concerned only with the difference JK . Since for all gases an elementary change in entropy is expressed by

$$dS = \frac{C_p dT}{T} - \left(\frac{dV}{dT} \right)_P dP,$$

and since, in the case under consideration, $dT=0$, we have

$$dS = - \left(\frac{dV}{dT} \right)_P dP.$$

If, therefore, a gas is compressed isothermally from zero pressure to pressure P the change in entropy is

$$S = - \int_0^P \left(\frac{dV}{dT} \right)_P dP.$$

For the actual gas this is represented by the line CJ while for the perfect gas it is represented by the line CK .

Assuming that the actual gas obeys the modified Berthelot equation of state, i.e.

$$PV = RT \left[1 + \frac{9PT_c}{128P_cT} \left(1 - 6 \frac{T_c^2}{T^2} \right) \right],$$

where T_c and P_c are the critical values of temperature and pressure, we have

$$\left(\frac{dV}{dT} \right)_P = \frac{R}{P} \left[1 + \frac{27}{32} \frac{PT_c^3}{P_cT^3} \right].$$

Hence

$$S_{JC} = CJ = - \int_0^P \frac{R}{P} \left[1 + \frac{27}{32} \frac{PT_c^3}{P_cT^3} \right] dP. \dots\dots\dots(1)$$

For the ideal gas, $PV = RT$ so that

$$\left(\frac{dV}{dT} \right)_P = \frac{R}{P},$$

and hence

$$S_{KC} = CK = - \int_0^P \frac{R}{P} dP. \dots\dots\dots(2)$$

The value of the entropy change accompanying a change from the actual state to the ideal state is thus given by

$$\begin{aligned} JK = S_{JO} - S_{KC} &= - \int_0^P \frac{27RT_c^3}{32T^3P_c} dP \\ &= - \frac{27}{32} \frac{RT_c^3P}{T^3P_c}. \end{aligned}$$

Hence

$$S^o = S + \frac{27RT_c^3P}{32T^3P_c}.$$

For oxygen $T_c = 154.28^\circ \text{C. abs.}$ and $P_c = 49.713 \text{ atm.}$ so that the correction is $\frac{27 \times 1.9869 \times 154.28^3 \times 1}{32 \times 90.13^3 \times 49.713} = 0.17 \text{ E.U.}$ The entropy at the point K is thus 40.74 E.U.

The extension of the entropy curve upwards in fig. 4 from the point K to the point L , where the temperature is $298.1^\circ \text{C. abs.}$, is again found by graphical integration using the experimentally determined values of C_p for this region. The increase in entropy found in this way is 8.28 E.U. , so that the entropy of the oxygen at a temperature of $298.1^\circ \text{C. abs.}$ and at a pressure of 1 atmosphere is 49.02 E.U.

Figure 6 shows the state changes for nitrogen again under a pressure of 1 atmosphere. It will be observed that there is only one transition in the solid state.

The advantage of expressing all the entropies of the gases dealt with

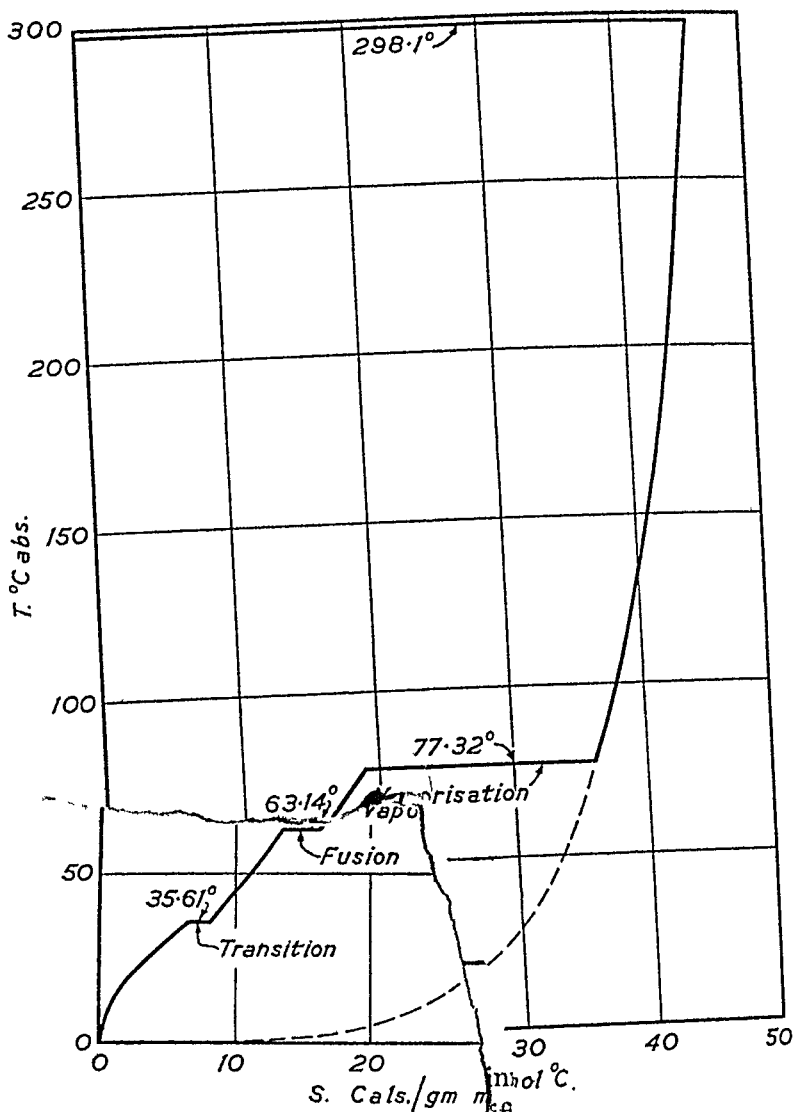


FIG. 6.

in combustion processes in the manner outlined above is that the entropies of a mixture of gases can now be correctly stated and if a chemical reaction occurs between the gases the changes in absolute entropy between the products and the original mixture can be calculated. This gives a considerably simplified method of determining equilibria constants for reactions. The absolute entropy of a mixture of gases of known composition may be found at any pressure and temperature from the entropy values given in the tables as shown by the following example.

The products of combustion in the clear cylinder have a total pressure of 400 lb./sq

in the tables as shown by

range volume of an engine
n.² abs. and a temperature

of $4000^{\circ}\text{F. abs.}$ The percentage volumetric composition of the undissociated gas mixture is CO_2 , 5.37; H_2O , 10.39; N_2 , 73.72 and O_2 , 10.52. It is required to find the absolute entropy of this gas mixture per pound mol.

The volumetric proportions are the same as the molal proportions. Figure 7 shows one pound mol of the mixture with the gases separated into proportional volumes as given by the analysis. The number of mols of the gases is as shown and if each gas is assumed to be at one atmosphere pressure and at a temperature of $4000^{\circ}\text{F. abs.}$, the entropy of the mixture is given by $\sum mS_T$, where m is the number of mols and S_T the entropy of each gas. The tables give, for one mol

of CO_2 , H_2O , N_2 and O_2 at $4000^{\circ}\text{F. abs.}$, the following values for S_T : 75.496; 64.624; 61.159 and 65.192, so that

$$\begin{aligned}\sum mS_T &= [0.0537 \times 75.496 + 0.1039 \times 64.624 + 0.7372 \times 61.159 \\ &\quad + 0.1052 \times 65.192] \\ &= 62.713 \text{ E.U.}\end{aligned}$$

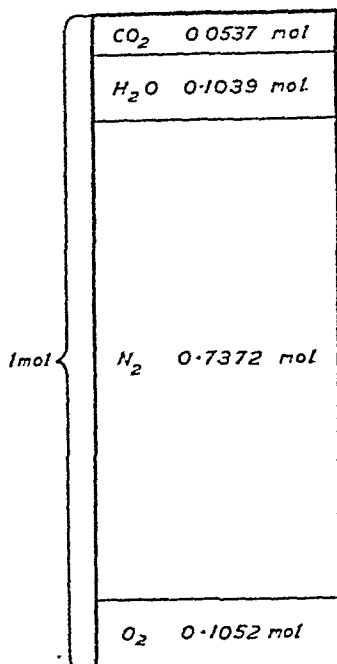


FIG. 7.

In the actual gas mixture, however, each gas, instead of occupying its own volume at the total pressure, occupies the full volume (i.e. the volume of one pound mol) at its partial pressure and hence, due to the irreversible expansion from the volumes shown in the diagram to the final volume, each gas increases its entropy by an amount which is determined as shown below. In the deduction use is made of the idea of semipermeable walls. A substance which is capable of allowing one gas to pass through it and yet blocks the passage of other gases is said to be semipermeable. It is found that glowing platinum sheet permits hydrogen to pass freely through it, but not other gases, while a porous membrane, soaked in water, permits any gas which is soluble in water, such as ammonia, to flow freely through it and excludes gases which are insoluble in water, such as hydrogen. Up till now semipermeable walls have not been discovered for all gases but the discussion which follows is based on the conception of such materials existing, and enables an expression for the entropy increase, due to the expansion of a gas in a gas mixture, to be determined. Use will also be made of

the properties of semipermeable walls when discussing the maximum work of a reaction. (See p. 23.)

Consider two of the gases to be separated by semipermeable pistons as shown in fig. 8, i.e. the right hand piston is permeable to gas *B* while the left hand piston is permeable to gas *A*. The pressure between the two pistons in the position shown is $2p_a$ and if the left hand piston is held fast while the excess pressure is allowed to act on the right hand piston this will move to the right and external work will be available.

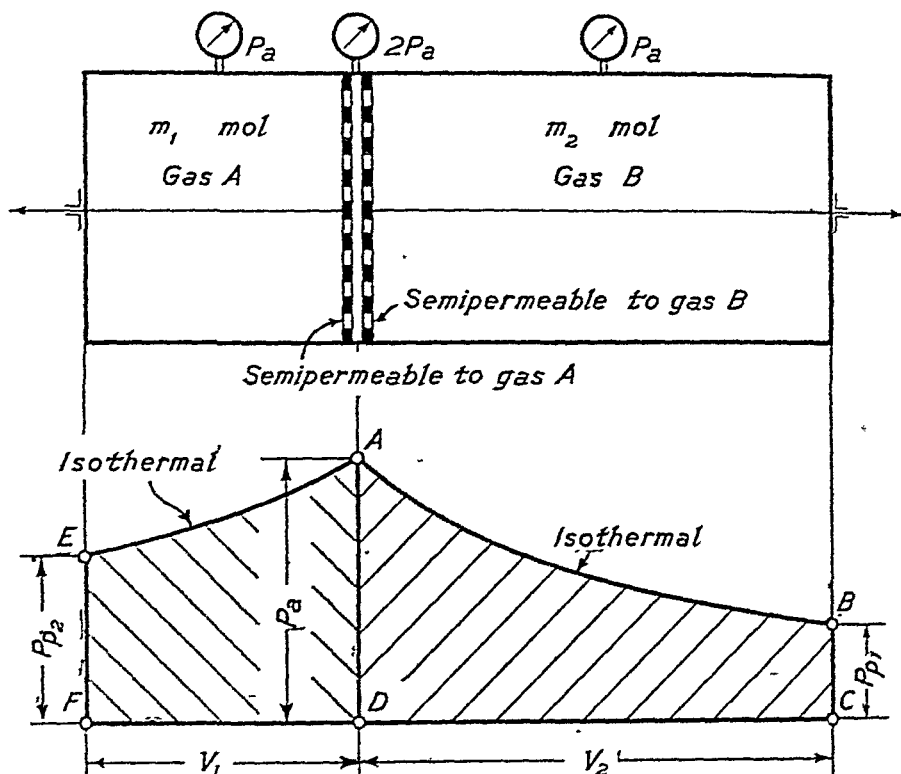


FIG. 8.

As the piston moves, gas *B* passes freely through its semipermeable wall so that it exerts no pressure on the piston. The gas *A* thus pushes this piston and performs work on it in the same way as would occur if the gas *B* were not present. With a slow enough motion of the piston the expansion may be made isothermal and reversible and the work performed is given by the area *ABCD* which is equal to

$$\frac{RTm_1}{J} \log_e \frac{V_1 + V_2}{V_1},$$

and since this equals the heat supplied at T the entropy change is

$$\frac{Rm_1}{J} \log_e \frac{V_1 + V_2}{V_1} = \frac{Rm_1}{J} \log_e \frac{p_a}{p_1}.$$

If now the left hand piston is released gas *B* performs work on it, the amount being the same as would occur if the gas *A* were absent. This is given by the area *AEFD* which is equal to

$$\frac{m_2 RT}{J} \log_e \frac{V_1 + V_2}{V_2} = \frac{m_2 RT}{J} \log_e \frac{p_a}{p_{r_2}},$$

and the corresponding increase in entropy is

$$\frac{m_2 R}{J} \log_e \frac{p_a}{p_{r_2}}.$$

If the total gas volume $V_1 + V_2$ is equal to 1 mol we have

$$\frac{p_a}{p_{r_1}} = \frac{1}{m_1}; \quad \frac{p_a}{p_{r_2}} = \frac{1}{m_2},$$

or, in general,

$$\frac{p_a}{p_r} = \frac{1}{m},$$

and hence the entropy increase due to the expansion of any single gas is

$$\frac{mR}{J} \log_e \frac{p_a}{p_r} = \frac{mR}{J} \log_e \frac{1}{m}.$$

Hence for the mixture of gases of the example the increase is

$$\begin{aligned} & \Sigma \frac{mR}{J} \log_e \frac{1}{m} \\ &= 1.987 \left[0.0537 \log_e \frac{1}{0.0537} + 0.1039 \log_e \frac{1}{0.1039} \right. \\ & \quad \left. + 0.7372 \log_e \frac{1}{0.7372} + 0.1052 \log_e \frac{1}{0.1052} \right] \\ &= 1.987 \times 0.854 \\ &= 1.697 \text{ E.U.} \end{aligned}$$

The total entropy at one atmosphere pressure and 4000° F. abs. is thus 62.713 + 1.697 = 64.410 E.U. The entropy is required, however, at 400 lb./in.² abs. (27.21 atm.) and 4000° F. abs. On the *PV* and *TS* diagrams (fig. 9) the state point of the gas mixture at 1 atmosphere pressure would be represented by the point *A*. In changing its state to the point *B*, which is at the same temperature, any path may be chosen in order to calculate the entropy change. The simplest path to choose is the reversible isothermal at 4000° F. abs. passing through *A* and *B*. The heat rejected is

$$\begin{aligned} & \frac{RT}{J} \log_e \frac{V_A}{V_B} = \frac{RT}{J} \log_e \frac{p_B}{p_A} \\ &= 1.987 \times 4000 \log_e \frac{27.21}{1} \text{ B.Th.U.} \\ &= 1.987 \times 4000 \times 3.304 \text{ B.Th.U.} \end{aligned}$$

This is equal to the area $ABDC$ on the TS field so that the entropy decrease is $1.987 \times 3.304 = 6.565$ E.U. The required entropy value of the gas mixture at the given conditions is thus $64.410 - 6.565 = 57.845$ E.U.

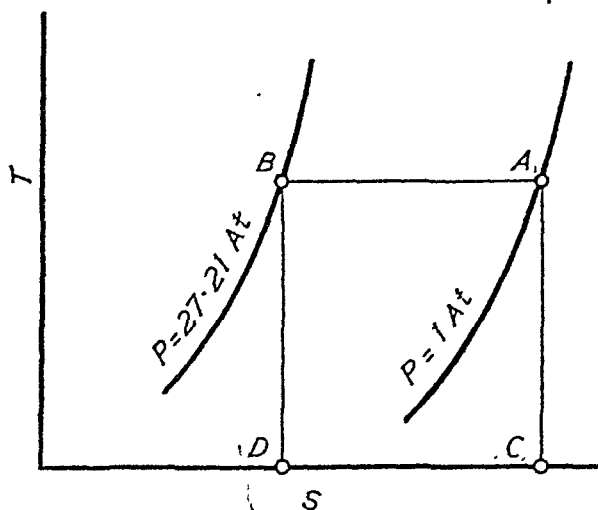
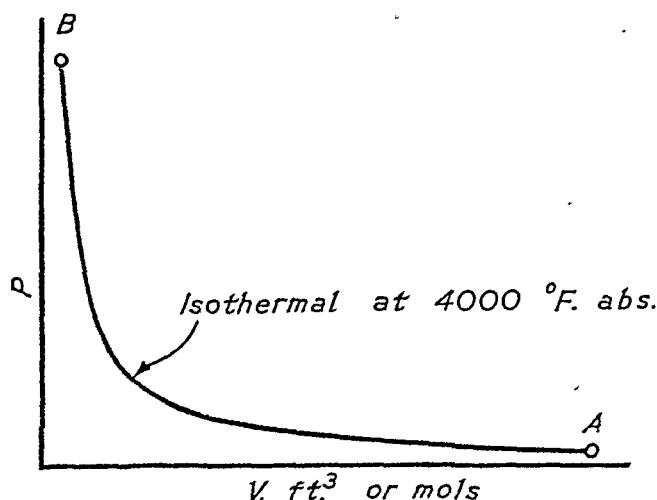


FIG. 9.

In determining the absolute entropy value of a gas or gaseous mixture the same procedure as outlined in the above example may be followed whatever the pressure, volume and temperature of the gas may be.

4. **Total Heat.** The total heat H of a gas is taken as the difference between the total heats of the gas at the temperature under consideration and the absolute zero temperature. If these total heats, which refer to the gas in the ideal or perfect gas state are denoted by H_T° and H_0° the total heats tabulated are equal to $H_T^\circ - H_0^\circ$. For a perfect

gas at absolute zero temperature H_0° is the same as the internal energy E_0° at that temperature so that the tabulated values of total heats are equal to $H_T^\circ - E_0^\circ$. The prefix 0 in these symbols denotes that the gas is in the ideal gaseous state. We have therefore for gases

$$H = H_T^\circ - E_0^\circ = \int_0^T C_p^\circ dT$$

where C_p° is the specific heat at constant pressure of the hypothetical gas already discussed in the previous paragraph. ($H_T^\circ - E_0^\circ$) is thus equal to the area below the hypothetical gas curve shown on the TS

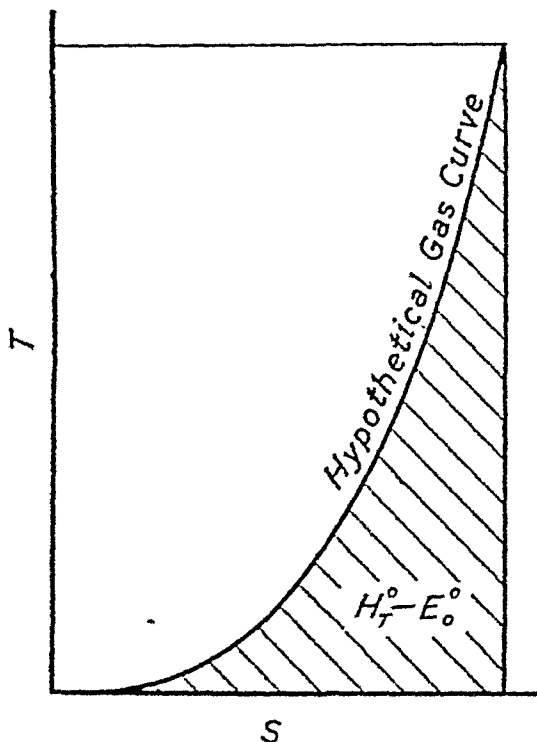


FIG. 10.

field in fig. 10 between 0° F. abs. and T° F. abs. A few skeleton values of $(H_T^\circ - E_0^\circ)$, at various temperature levels, are given in the original work of the physicists and it is from these that the values shown in the tables of this volume are deduced. Over limited ranges of temperature it is permissible to write

$$C_p = A + BT + CT^2,$$

where A , B and C are constants. Solving for the constants over one of these limited temperature ranges enable intermediate values of $(H_T^\circ - E_0^\circ)$ to be calculated. By covering the complete temperature

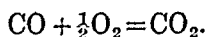
range from 400° F. abs. to the upper limits of 5400° F. abs. or 9000° F. abs. with these zones entirely satisfactory agreement with the original values was maintained.

5. Internal Energy. The internal energy, $E = (E_T^{\circ} - E_0^{\circ})$, at any temperature T , is found from the total heat $(H_T^{\circ} - E_0^{\circ})$ by means of the relationship

$$\begin{aligned}(E_T^{\circ} - E_0^{\circ}) &= (H_T^{\circ} - E_0^{\circ}) - \frac{R}{J} T \\ &= (H_T^{\circ} - E_0^{\circ}) - 1.9869T.\end{aligned}$$

6. Lower Heats of Reaction (H_p). The engineer uses the word "lower" in referring to heats of reaction only when dealing with the combustion of hydrogen or fuels containing hydrogen, because at room temperature hydrogen is the only constituent forming a vapour which condenses. Since the physicists, however, have reduced the gases to the hypothetical gaseous state for which no condensation can occur, even when very low temperatures are considered, the heats of reaction for all gases must be referred to as "lower" heats of reaction.

The lower heat of reaction plays an important part in dissociation calculations and it has to be observed that the heat of reaction of a fuel depends upon the temperature at which the reaction occurs. Thus, if carbon monoxide is burned at constant pressure the heat given to the surroundings, under isothermal reaction conditions, is the constant pressure heat of reaction at room temperature. If, however, the reaction were to occur at some higher temperature the heat given up, i.e. the heat of the reaction, will have a different value from that at room temperature. This is due to the change which occurs in the difference of the total heats between the products and reactants as the temperature of the surroundings is altered. The point is made clear by considering the combustion of carbon monoxide. In burning one mol of carbon monoxide at a temperature of 600° F. abs. the heat of reaction is found to be 121794 B.Th.U. as given in the tables on page 93. The reaction proceeds in accordance with the reaction equation,



The sum of the total heats $H_T - E_0$ of the reactants, i.e. of 1 mol. of CO and $\frac{1}{2}$ mol of O_2 at 600° F. abs. is $4173 + \frac{1}{2} \times 4168 = 6257$ B.Th.U. and of the products (i.e. of 1 mol of CO_2), 4626 B.Th.U. The difference between the total heats of the reactants and products is thus $6257 - 4626 = 1631$ B.Th.U. and this makes the heat of reaction larger than it would have been had there been no difference in these total heats. If now the reaction proceeds at 5000° F. abs. the difference in the total heats of the reactants and the products is $40449 + \frac{1}{2} \times 42123 - 64132$

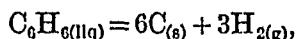
$= -2621$ B.Th.U. The heat of reaction is thus 2621 B.Th.U. less than it would have been if there were no difference between the total heats of the reactants and products. The heat of reaction of CO at 5000° F. abs. is thus less than that at 600° F. abs. by the amount $1631 + 2621 = 4252$ B.Th.U. and this equals the difference in the H_p values of CO as given in the tables at 600° F. abs. and 5000° F. abs. Since the values of $(H_T^{\circ} - E_0^{\circ})$ are zero for all gases at 0° F. abs. there is no difference between the total heats of the reactants and products at this temperature and the heat of reaction, which is denoted by ΔE_0° , is the same as would be obtained at any other temperature provided the total heats of the reactants and the products were equal. Since, in almost all cases, there is a difference in the total heats and this difference is given by $\Delta(H_T^{\circ} - E_0^{\circ})$, the true heat of reaction at any temperature is $\Delta E_0^{\circ} + \Delta(H_T^{\circ} - E_0^{\circ})$. For CO, $\Delta E_0^{\circ} = 120163$ B.Th.U./lb. mol so that at 600° F. abs. $H_p = 120163 + 1631 = 121794$ B.Th.U./lb. mol as given in the tables. Similarly at 5000° F. abs. $H_p = 120163 - 2621 = 117542$ B.Th.U./lb. mol, as also given in the tables.

It frequently happens that it is not possible to find, by direct means, the heat of reaction of a fuel. In this case it is necessary to apply Hess's law, which states that the heat liberated by a reaction is independent of the path pursued between the initial and final states. If, for example, carbon is burned directly to form carbon dioxide the heat liberated is the same as would be the case if the carbon were first burned to carbon monoxide followed by burning of the carbon monoxide to carbon dioxide.

We shall illustrate the application of the law by determining the heat of reaction of benzene vapour (C_6H_6) at a temperature of 600° F. abs. The heat of reaction of benzene liquid can be found by first considering the liquid to be separated out to solid carbon and gaseous hydrogen. The carbon is then burned to CO_2 and the hydrogen to H_2O so that by applying Hess's law to these reactions we find the heat liberated in burning liquid benzene to gaseous CO_2 and gaseous H_2O . If benzene vapour had been burned instead of the liquid the latent heat required for evaporation of the liquid would not have been demanded from the fuel so that the heat of reaction of the vapour must be greater than that of the liquid by this amount. Finally, if all these operations occur at the usual temperature at which the heats are quoted, namely 537° F. abs. (25° C.), the heat of reaction at 600° F. abs. must be calculated by taking into account the difference in total heats between the reactants and products at 537° F. abs. and 600° F. abs.

Pitzer ⁽¹⁷⁾ has supplied the necessary data to enable a calculation of the heat of reaction of benzene vapour to be carried out on the above lines.

When splitting up liquid benzene to solid carbon and gaseous hydrogen, as shown by the reaction equation,

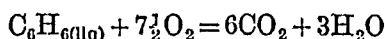


the heat liberated at 537° F. abs. is 20,160 B.Th.U./lb. mol. (See Parks.⁽¹⁸⁾) To find the heat of reaction of C burned to CO₂ we require the total heat of solid carbon, of gaseous O₂ and of gaseous CO₂ at 537° F. abs. These are given as 251, 2069 and 2240 cal./gm. mol while the heat of reaction at absolute zero temperature is 93949 cal./gm. mol. We thus have the heat of reaction for the combustion of carbon to carbon dioxide (C + O₂ = CO₂) at 298.1° C. abs. (25° C.) as

$$\begin{aligned}\Delta H &= 251 + 2069 + 93949 - 2240 \\ &= 94029 \text{ cal./gm. mol} \\ &= 169252 \text{ B.Th.U./lb. mol.}\end{aligned}$$

The table on p. 94 shows that the heat of reaction of H₂ + ½ O₂ = H₂O at 537° F. abs. is 104009 B.Th.U./lb. mol.

From the reaction equation



we obtain the heat liberated at constant pressure

$$\begin{aligned}H_{p(537)} &= 20160 + 6 \times 169252 + 3 \times 104009 \\ &= 1347699 \text{ B.Th.U./lb. mol.}\end{aligned}$$

Matthews⁽¹⁹⁾ gives the latent heat of benzene as

$$L = 107.05 - 0.1581\theta \text{ cal./gm.}$$

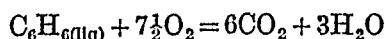
where θ is the temperature in ° C., so that at 25° C.

$$\begin{aligned}L &= 107.05 - 3.95 \\ &= 103.1 \text{ cal./gm.} \\ &= 8045.4 \text{ cal./gm. mol} \\ &= 14481 \text{ B.Th.U./lb. mol.}\end{aligned}$$

The value of H_p for benzene vapour is therefore (at 537° F. abs.)

$$14481 + 1347699 = 1362180 \text{ B.Th.U./lb. mol}$$

and at 600° F. abs. with



it becomes

$$\begin{aligned}H_{p(600)} &= 1362180 + (H_{600} - H_{537})_{\text{C}_6\text{H}_6} + 7\frac{1}{2}(H_{600} - H_{537})_{\text{O}_2} \\ &\quad - 6(H_{600} - H_{537})_{\text{CO}_2} - 3(H_{600} - H_{537})_{\text{H}_2\text{O}} \\ &= 1362180 + 1312 + 3359 - 3391 - 1508 \\ &= 1361952 \text{ B.Th.U./lb. mol.}\end{aligned}$$

The corresponding value at constant volume is

$$\begin{aligned}H_{v(600)} &= 1361952 + \frac{1}{2}RT/J \\ &= 1361952 + 596 \\ &= 1362548 \text{ B.Th.U./lb. mol.}\end{aligned}$$

since, under constant pressure conditions, there is an increase in volume amounting to $\frac{1}{2}$ mol per mol of fuel burned.

In the next paragraph the maximum work of a reaction is discussed and, as shown by Nernst, this maximum work is equal to the heat of reaction ΔE_0° at absolute zero temperature.

7. Maximum Work of Reaction and Equilibrium Constant. In applying the second law of thermodynamics to determine the maximum available work obtainable from a heat engine the discussion shows that this maximum is a function of the temperature range within which the working substance operates and further that this work is independent of the working substance. In the treatment, however, as usually given, only physical changes in the working substance are considered and all operations are regarded as reversible. When the combustion processes occurring in an engine are considered it would appear, at first sight, to be impossible to regard these as reversible, and hence it would appear to be impossible to determine the value of the maximum work attainable from a reaction. A conceivable method, however, can be pictured of a reaction process occurring in which all operations are reversible and from which work is obtainable, so that by applying the same arguments to the process as is normally done to reversible physical changes it is found that the work obtained from the reaction has a maximum value. This method, which enables an expression for the maximum work of reaction to be established, was suggested by van't Hoff and is illustrated by the van't Hoff equilibrium box.

In fig. 11 the vessel *A* is a reaction chamber of very large capacity maintained at constant temperature *T* by the surroundings. The reactants, taken in this case to be CO and O₂, are contained in the vessels *B* and *C* at the constant pressure *p* (in this preliminary discussion) and small quantities of these can be supplied, in the correct proportions for combustion, to the reaction chamber. Before entering the chamber, however, each gas is expanded isothermally in a motor to the partial pressure exerted by the gas in the reaction chamber. Work is thus rendered available, the amounts being, per mol of CO consumed,

$$pv \log_e \frac{p}{p_{\text{CO}}} \quad \text{and} \quad \frac{1}{2}pv \log_e \frac{p}{p_{\text{O}_2}},$$

where *v* is the volume of the pound mol, *p*_{CO} is the partial pressure of the CO and *p*_{O₂} the partial pressure of the O₂. As shown in the diagram the CO and O₂ gases are enabled to enter the reaction chamber because semipermeable walls, suitable for each gas, are fitted between the motors and the reaction chamber. The CO₂ formed by the reaction in vessel *A* escapes, as soon as it is formed, through the semipermeable

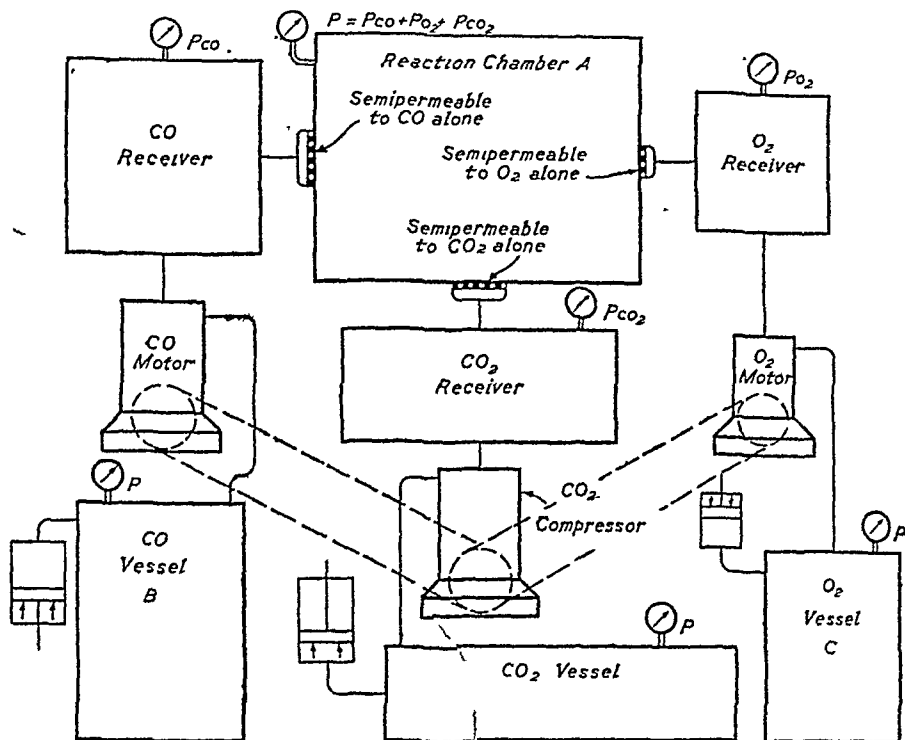


FIG. 11.

wall shown, to the CO₂ receiver, while the heat of the reaction is absorbed by the surroundings so that the process is isothermal and reversible. The discharged CO₂ is compressed isothermally from its pressure p_{CO_2} to the original pressure p of the reactants. The expenditure of work required for this is

$$pv \log_e \frac{p}{p_{CO_2}}.$$

The net gain in work is thus, in heat units,

$$\begin{aligned} & \frac{pv}{J} \log_e \frac{p}{p_{CO}} + \frac{1}{2} \frac{pv}{J} \log_e \frac{p}{p_{O_2}} - \frac{pv}{J} \log_e \frac{p}{p_{CO_2}} \\ &= \frac{RT}{J} \log_e \frac{p}{p_{CO}} \times \frac{p^{\frac{1}{2}}}{p_{O_2}^{\frac{1}{2}}} \times \frac{p_{CO_2}}{p} \\ &= \frac{RT}{J} \log_e p^{\frac{1}{2}} \frac{p_{CO_2}}{p_{CO} \times p_{O_2}^{\frac{1}{2}}} \dots \dots \dots (1) \end{aligned}$$

All operations in the above reaction process are reversible since it is only necessary to return CO₂ to the reaction chamber and let heat flow in from the surroundings to enable the CO₂ to be split up to CO and O₂ and these are then returned to their original vessels. The work done, as given by equation (1), is thus a maximum for the reaction

$\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$ occurring at the constant temperature T and constant pressure p . If now, at this same temperature T and pressure p , a new set of conditions should exist in the reaction chamber so that the partial pressures of the reactants and products become p'_{CO} , p'_{O_2} , and p'_{CO_2} , the same arguments shown above lead to the expression

$$\frac{RT}{J} \log_e p^{\frac{1}{2}} \frac{p'_{\text{CO}_2}}{p'_{\text{CO}} \times p'_{\text{O}_2}{}^{\frac{1}{2}}}$$

for the maximum work of reaction. Here also all operations are reversible so that this must equal the expression given in equation (1) as otherwise it would be possible to generate a continuous supply of energy merely by allowing the reaction showing the greater work to drive the one showing the lesser when this acts in the reverse direction. Hence

$$\frac{p_{\text{CO}_2}}{p_{\text{CO}} \times p_{\text{O}_2}{}^{\frac{1}{2}}} = \frac{p'_{\text{CO}_2}}{p'_{\text{CO}} \times p'_{\text{O}_2}{}^{\frac{1}{2}}} = K_p \dots \dots \dots (2)$$

is a constant known as the equilibrium constant. In any mixture of gases in which CO , O_2 and CO_2 are present alone or with other gases at the temperature T and total pressure p , the three gases CO , O_2 and CO_2 must, under equilibrium conditions, have partial pressures which satisfy the relationship given by equation (2), otherwise it would be possible for work to be done on or by any of these constituents and the mixture would not then be in equilibrium. If the reactants and products are not initially and finally all at the pressure p it becomes necessary to add or deduct the isothermal works of expansion or compression to or from equation (1) in order to find the maximum work of reaction. The value of K_p is, however, unaffected by these changes. It is customary to take the pressure p , appearing in equation (1), as one atmosphere so that the maximum work of reaction becomes $\frac{RT}{J} \log_e K_p$ with the partial pressures expressed in atmospheres. It has to be observed that this maximum work does not include the work done on or by the gases due to a difference between the sum of the mols of the reactants and the products. The cylinders shown attached to the receivers in fig. 11 indicate that for the combustion of CO with O_2 this work amounts to

$$\frac{pv}{J} + \frac{\frac{1}{2}pv}{J} - \frac{pv}{J} = \frac{1}{2} \frac{pv}{J} \text{ or } \frac{1}{2} \frac{RT}{J}.$$

8. Free Energy. In the last paragraph it was shown that the maximum work of a reaction is given by $\frac{RT}{J} \log_e K_p$, where K_p is the equilibrium constant and is a function of the partial pressures of the

reactants and products of the reaction. In order to calculate the value of K_p , the following method due to Willard Gibbs and developed by Lewis will now be considered.

If the total heat, absolute entropy and absolute temperature of a hypothetically ideal gas be denoted by H_T , S_T and T we can write down a function F_T in terms of these as

$$F_T = H_T - TS_T.$$

Since H_T and TS_T are state functions it follows that this new function, known as the thermodynamic potential or free energy, is itself a state function. If now we denote this function for two states A and B of a substance by $(F_T)_A$ and $(F_T)_B$ we have, for an isothermal change,

$$(F_T)_A - (F_T)_B = \Delta F_T = \Delta H_T - \Delta TS_T = \Delta H_T - T \Delta S_T$$

where $\Delta H_T = (H_T)_A - (H_T)_B$ and $\Delta S_T = (S_T)_A - (S_T)_B$.

If the change is reversible $T \Delta S_T$ is the heat added and is denoted by Q say. We thus have

$$\Delta F_T = \Delta H_T - Q = \Delta E_T + \Delta PV - Q. \dots\dots\dots(1)$$

and if we regard the change as occurring at constant pressure as well as at constant temperature, $\Delta PV = P \Delta V$, which is the work done against the pressure P due to the change in volume ΔV . Rewriting equation (1) as

$$Q = \Delta E_T + (P \Delta V - \Delta F_T), \dots\dots\dots(2)$$

and comparing it with the energy law, i.e. heat supplied = change in internal energy + work done, we see that $-\Delta F_T$ represents the maximum work of the state change apart from that due to a change in volume. It is impossible for the maximum work obtainable to be any more or less than $-\Delta F_T$ and this applies to any reversible process in which the state changes from A to B . Thus, as quoted by Lewis and Randall, consider the action of aqueous sulphuric acid upon zinc under constant atmospheric pressure in a thermostat. Under normal conditions the reaction is highly irreversible and the only work performed is that due to the formation of hydrogen which has to expand against atmospheric pressure. If, however, the same substances are arranged as a galvanic cell in the thermostat with zinc as one electrode and a reversible hydrogen electrode as the other and if the two electrodes are connected externally to an electric motor so as to utilise the electrical energy now available, work will be performed and this will be a maximum if the opposing E.M.F. differs only by an infinitesimally small amount from that generated by the cell. Simultaneously with the production of electrical work zinc enters into solution at the zinc electrode and

hydrogen is evolved at the hydrogen electrode. The work performed will be a maximum because, by subsequent reduction of the opposing E.M.F. below that of the cell, hydrogen is consumed and zinc precipitated so that the process is reversible. Hence the net work available under electrical conditions is given by

$$(A_A - A_B) - P\Delta V$$

where $(A_A - A_B)$ is the external electrical work performed. From equation (2) the maximum work is $-\Delta F_T$ so that

$$-\Delta F_T = (A_A - A_B) - P\Delta V.$$

Hence for any process occurring at constant temperature and pressure,

$$-\Delta F_T = (F_T)_A - (F_T)_B \dots\dots\dots (3)$$

is the maximum work which is available and applied usefully. For this reason F is called the free energy.

It has to be noted particularly that the work $-\Delta F$ of a reaction is not necessarily the same as the heat of the reaction. As shown by Nernst the two are equal at absolute zero temperature and will also be equal at any given temperature if the heat capacity, reckoned from absolute zero, of the reactants is the same as that of the products and if the sum of the entropies of the reactants is the same as that of the products. It has been shown that the maximum work of a reaction is given by the change in free energy, but no reference has been made as to how this change is computed. Since the thermal magnitudes are reckoned from absolute zero temperature, the change in free energy for a reaction must include the change in free energy at absolute zero temperature and this is equal to $-\Delta E_0$. Hence the maximum work is given by the expression

$$-\Delta E_0 - \Delta(F_T - E_0)$$

and, since this is the same as the work available in the van't Hoff equilibrium box, we have

$$\frac{RT}{J} \log_e K_p = -\Delta E_0 - \Delta(F_T - E_0)$$

or

$$\frac{R}{J} \log_e K_p = -\Delta E_0/T - \Delta(F_T - E_0)/T.$$

The function $-\frac{(F_T - E_0)}{T} = -\frac{F}{T}$ is given in the tables as also ΔE_0 so that the value of $\log_e K_p$ is calculable. As an example, we choose the combustion of carbon monoxide with oxygen to form carbon dioxide at a temperature of 600° F. abs. The sum of the free energy functions of the reactants CO and $\frac{1}{2}\text{O}_2$ is $-41.149 - \frac{1}{2} \times 42.871 = -62.585$

B.Th.U./lb. mol \times° F. while the free energy function of the CO_2 is -44.394 B.Th.U./lb. mol \times° F. The change is thus

$$-62.585 + 44.394 = -18.191 \text{ B.Th.U./lb. mol } \times^{\circ} \text{ F.}$$

Also the heat of reaction $-\Delta E_0$ of CO at 0° F. abs. is given as 120163 B.Th.U./lb. mol so that

$$-\frac{\Delta E_0}{T} = 120163/600 = 200.272 \text{ B.Th.U./lb. mol. } \times^{\circ} \text{ F.}$$

We thus have

$$\frac{R}{J} \log_e K_p = 200.272 - 18.191 = 182.081,$$

and hence

$$\log_{10} K_p = 182.081/1.987 \times 2.303 \\ = 39.80$$

and

$$K_p = 6.3096 \times 10^{39}$$

as given in the tables.

EXAMPLES ON THE USE OF THE TABLES

EXAMPLE 1

Flue gases leave a boiler at a temperature of 600° F. and have the fractional composition: O_2 , 0.098; N_2 , 0.799; CO_2 , 0.098 and H_2O , 0.005. This composition gives an apparent molecular weight of 29.91. It is required to find the heat given up by 1 lb. of these gases if cooled to a temperature of 80° F. at constant pressure. Assume that the H_2O remains in the gaseous state down to 80° F.

The total heat of the mixture has to be calculated at 600° F. (1060° F. abs.) by multiplying the number of mols of each constituent by its total heat at 1060° F. abs. and summing the results so obtained. This procedure has to be repeated at 80° F. (540° F. abs.). The difference between these quantities then gives the heat liberated.

Arranging the work in tabular form we have at $T = 1060^{\circ}$ F. abs. :

Gas	Vol. or No. of mols (m)	H_{1060}	mH_{1060}
O_2	0.098	7549	739.8
N_2	0.799	7416	5925.5
CO_2	0.098	9378	919.0
H_2O	0.005	8636	43.2
		$\Sigma mH_{1060} = 7627.5$	

and at $T=540^{\circ}$ F. abs. :

Gas	m	H_{540}	mH_{540}
O ₂	0.098	3751	367.6
N ₂	0.799	3753	2998.7
CO ₂	0.098	4088	400.6
H ₂ O	0.005	4318	21.6
		$\Sigma mH_{540}=3788.5$	

The difference in total heat is thus

$$7627.5 - 3788.5 = 3839.0 \text{ B.Th.U./lb. mol}$$

and since the apparent molecular weight of the flue gases is 29.91 the heat given up per pound is

$$3839.0/29.91 = 128.4 \text{ B.Th.U.}$$

EXAMPLE 2

The products of combustion of a petrol engine, supplied with 20 per cent. excess air, have the following volumetric analysis: N₂, 0.7466; O₂, 0.0329; CO₂, 0.1084; H₂O, 0.1121. This gives an apparent molecular weight of 28.75 and gas constant $R=53.70$. If the tempera-

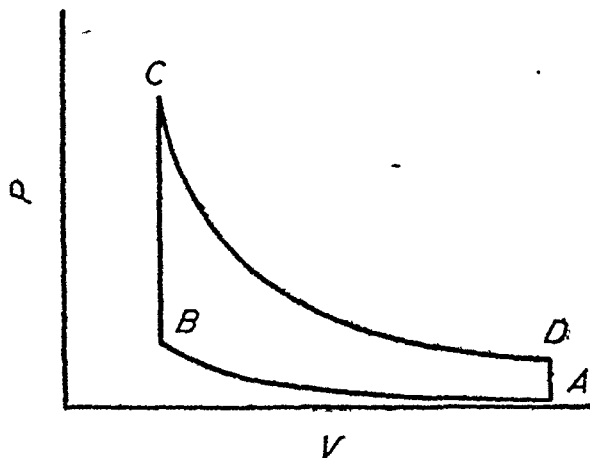


FIG. 12.

ture of the charge at the beginning of compression is 100° F. and the compression ratio of the engine is 5, it is required to find the ideal thermal efficiency of the engine. The calorific value of the petrol used is 20,300 B.Th.U./lb. and its gravimetric composition is 85.3 per cent. carbon and 14.7 per cent. hydrogen.

In determining the ideal efficiency, it is permissible to assume that the working substance consists of the products of combustion through-

out the complete cycle. The ideal cycle consists of isentropic compression (AB in fig. 12), constant volume burning (BC), isentropic expansion (CD) and constant volume cooling (DA).

In order to find the temperature at B , a value is first assumed and if correct, it will be found that the entropy at B is the same as at A . If this agreement is not obtained the process is repeated until the condition is satisfied.

Denoting the pressures at A and B by p_A and p_B , we have, for the entropy at A ,

$$S_A = \sum m(S_T)_A + \sum m \frac{R}{J} \log_e \frac{1}{p_p} + \frac{R}{J} \log_e \frac{1}{p_A}, \dots\dots\dots(1)$$

where, for each constituent, m is the number of mols, $(S_T)_A$ is the entropy at a pressure of 1 atmosphere and p_p the partial pressure (in atmospheres) when the pressure of the mixture is 1 atmosphere. p_A is the total pressure (in atmospheres) of the gas mixture at A . The first term on the right of equation (1) represents the entropy of the gas mixture with each constituent at a pressure of 1 atmosphere (as given by the tables). The second term is the correction necessary to bring the mixture to a pressure of 1 atmosphere so that each constituent is subjected to a reduction in pressure from 1 atmosphere to its own partial pressure p_p . The third expression gives the necessary correction to bring the mixture from 1 atmosphere pressure to p_A the pressure at A . In the same way the entropy at B is given by the expression

$$S_B = \sum m(S_T)_B + \sum m \frac{R}{J} \log_e \frac{1}{p_p} + \frac{R}{J} \log_e \frac{1}{p_B} \dots\dots\dots(2)$$

The second terms on the right of equations (1) and (2) are equal so that the difference in entropy between the state points A and B is given by the expression

$$S_A - S_B = \sum m(S_T)_A - \sum m(S_T)_B + \frac{R}{J} \log_e \frac{p_B}{p_A};$$

but

$$\frac{p_B}{p_A} = r_c \text{ in } \frac{T_B}{T_A} \text{ No. ratio, } \frac{V_A}{V_B}.$$

where r_c is the compression ratio,

This gives

$$\begin{aligned} S_A - S_B &= \sum m(S_T)_A - \sum m(S_T)_B + \frac{R}{J} \log_e r_c \frac{T_B}{T_A} \\ &= \sum m(S_T)_A + \frac{R}{J} \log_e \frac{r_c}{T_A} - \sum m(S_T)_B + \frac{R}{J} \log_e T_B. \dots\dots\dots(3) \end{aligned}$$

The first two terms on the right remain constant for all assumed values of T_B so that it is advisable to determine their sum independently and equate this to the last two terms. Arranging the work in tabular form, we have

Gas	Vol. or mols (m)	S_{560}	mS_{560}
N ₂	0.7466	46.067	34.41
O ₂	0.0329	49.299	1.62
CO ₂	0.1084	51.452	5.58
H ₂ O	0.1121	45.452	5.09
			$\Sigma mS_{560} = 46.70$

The second term in equation (3) is $\frac{R}{J} \log_e \frac{r_c}{T_A}$

$$= 1.986 \times 2.303 \log_{10} 5/560$$

$$= -9.371 \text{ E.U.}$$

The first two terms in equation (3) are thus equal to $46.70 - 9.37 = 37.33$ E.U. and this must equal

$$\Sigma m(S_T)_B - \frac{R}{J} \log_e T_B.$$

For $\Sigma m(S_T)_B$ it is convenient again to arrange the work in tabular form with an assumed temperature of $T_B = 1000^\circ \text{ F. abs.}$:

Gas	m	S_{1000}	mS_{1000}
N ₂	0.7466	50.158	37.44
O ₂	0.0329	53.533	1.76
CO ₂	0.1084	57.284	6.21
H ₂ O	0.1121	50.257	5.63
			$\Sigma mS_{1000} = 51.04$

and $\frac{R}{J} \log_e T_B = 1.986 \times 2.303 \log_{10} 1000$

$$= 13.72.$$

Hence

$$\Sigma mS_{1000} - \frac{R}{J} \log_e T_B$$

$$= 51.04 - 13.72$$

$$= 37.32$$

as against 37.33 for the first two terms so that the assumed temperature for T_B of $1000^\circ \text{ F. abs.}$ may be accepted. The corresponding value of the internal energy E_2 at the point B is found by multiplying the number of mols of each constituent in the products by its internal

energy value as given in the tables at 1000° F. abs. and summing the products. It is convenient to carry out the calculation in tabular form as follows :

Gas	m	E_{1000}	mE_{1000}
N ₂	0.7466	4998	3731.5
O ₂	0.0329	5104	167.9
CO ₂	0.1084	6722	728.7
H ₂ O	0.1121	6130	687.2
			$E_2 = \Sigma mE_{1000} = 5315.3$

In order to find the temperature T_2 at the end of the constant volume burning period, its value is first assumed and the internal energy E_2 of the products calculated. If this is found to equal $E_2 + Q$, i.e. the internal energy at the point B plus the heat added per lb. mol, then the assumed temperature is correct. If not, the process is repeated until the condition is satisfied. From the data supplied in the statement of the problem it can be shown that the weight of the products of combustion per lb. of petrol is 18.85 lb. so that the heat added is

$$Q = 20,304 \times 28.75 / 18.85 = 30964 \text{ B.Th.U./lb. mol.}$$

If now we assume T_2 to be 5200° F. abs. the value of E_3 is found as follows :

Gas	m	E_{5200}	mE_{5200}
N ₂	0.7466	31560	23563
O ₂	0.0329	33680	1108
CO ₂	0.1084	56796	6156
H ₂ O	0.1121	45907	5146
			$E_3 = \Sigma mE_{5200} = 35973$

Since this is less than the required value of 36279 the assumed temperature of 5200° F. abs. for T_2 is too low. By further trial and error the required value of T_2 is found to be 5238° F. abs. and the corresponding value of E_2 is 36280 B.Th.U./lb. mol.

The entropy of the gaseous mixture at C must be the same as at D so that the temperature at D has to be found, by trial and error, until this condition is satisfied. The calculation is similar to that carried out during compression so that the detailed method does not require to be repeated. It is found that the required temperature at D is 3500° F. abs. and the corresponding value of E_D is 22683 B.Th.U./lb. mol. At $T_A = 560°$ F. abs. the value of E_A is 2887 B.Th.U./lb. mol.

The efficiency is given by the expression

$$\begin{aligned}\eta &= \frac{(E_C - E_B) - (E_D - E_A)}{(E_C - E_B)} \\ &= 1 - \frac{(E_D - E_A)}{Q} \\ &= 1 - \frac{22683 - 2887}{30964} \\ &= 0.361.\end{aligned}$$

EXAMPLE 3

A nozzle is supplied with air at a pressure of $62.0 \text{ lb./in.}^2 \text{ abs.}$ and temperature of $1600^\circ \text{ F. abs.}$ If the rate of air flow is 10 lb./sec. and the pressure at outlet from the nozzle is $14.7 \text{ lb./in.}^2 \text{ abs.}$, find the throat and exit areas. Assume that expansion to the throat is isentropic and that the frictional loss, for the complete expansion between inlet to and outlet from the nozzle is 15 per cent. of the isentropic heat drop. Assume also that the composition of the air by volume is O_2 , 21 per cent. and N_2 , 79 per cent. so that the molecular weight is 28.84 and the gas constant is 53.53.

It is necessary to find the mean isentropic index of expansion γ between the nozzle inlet and throat. The critical pressure ratio (r_c) is given by

$$r_c = \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}} \dots \dots \dots (1)$$

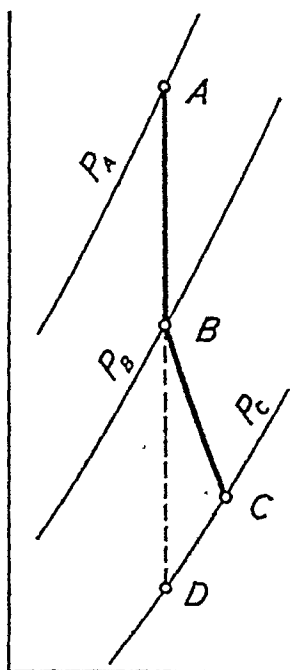


FIG. 13.

and if γ is taken provisionally as 1.4 we have $r_c = 0.53$ so that the throat pressure is nearly $0.53 \times 62.0 = 32.9$, say 33 lb./in.² abs. and the corresponding temperature is $T_B = T_A r_c^{\frac{\gamma-1}{\gamma}} = 1334.5^\circ \text{F. abs.}$ The mean value of γ between A and B in fig. 13 (where A represents the state point of the air at the nozzle inlet and B at the throat) can be found, when T_B is known, from the relationship

$$T_A/T_B = (p_A/p_B)^{\frac{\gamma-1}{\gamma}} \dots\dots\dots (2)$$

and the critical pressure ratio can then be found from equation (1). The entropy of 1 mol of air at A is given by the expression (see p. 30)

$$\sum m S_{\text{rev}} + \sum m \frac{R}{J} \log_e \frac{1}{m} + \frac{R}{J} \log_e \frac{1}{p_1},$$

where m is the fractional number of mols of the gases, oxygen and nitrogen. The corresponding expression for the entropy at B is

$$\Sigma m S_{1324.5} + \Sigma m \frac{R}{J} \log_e \frac{1}{m} + \frac{R}{J} \log_e \frac{1}{p_B}.$$

Since the entropies at A and B are equal, we have

$$\begin{aligned} \Sigma m S_{1600} + \Sigma m \frac{R}{J} \log_e \frac{1}{m} + \frac{R}{J} \log_e \frac{1}{p_A} \\ = \Sigma m S_{1324.5} + \Sigma m \frac{R}{J} \log_e \frac{1}{m} + \frac{R}{J} \log_e \frac{1}{p_B}, \end{aligned}$$

so that

$$\Sigma m S_{1600} - \Sigma m S_{1324.5} = \frac{R}{J} \log_e \frac{p_A}{p_B}.$$

Since m for O_2 is 0.21 and for N_2 , 0.79, we have

$$\begin{aligned} 0.21(S_{1600})_{O_2} + 0.79(S_{1600})_{N_2} - 0.21(S_{1324.5})_{O_2} - 0.79(S_{1324.5})_{N_2} \\ = \frac{R}{J} \log_e \frac{62.0}{p_B} \end{aligned}$$

from which p_B is calculable.

From the tables $(S_{1600})_{O_2} = 57.240$; $(S_{1600})_{N_2} = 53.617$; $(S_{1324.5})_{O_2} = 55.769$ and $(S_{1324.5})_{N_2} = 52.252$.

Hence

$$\begin{aligned} \frac{R}{J} \log_e \frac{62.0}{p_B} &= 0.21(57.240 - 55.769) + 0.79(53.617 - 52.252) \\ &= 1.3874; \\ \log_{10} \frac{62.0}{p_B} &= \frac{1.3874}{1.987 \times 2.303} = 0.30336; \\ p_B &= 30.833. \end{aligned}$$

It has to be remembered that these values of $p_B = 30.833$ lb./in.² abs. and $T_B = 1334.5^\circ$ F. abs. are not the true values at the throat, but they are on the isentropic curve passing through A and so the mean index γ found from them must be nearly correct.

From equation (2) we now have

$$\frac{1600}{1334.4} = \left(\frac{62.0}{30.833} \right)^{\frac{\gamma-1}{\gamma}}$$

from which $\gamma = 1.351$.

The critical pressure ratio is thus

$$\begin{aligned} r_c &= \left(\frac{2}{1.351} \right)^{\frac{1.351}{0.251}} \\ &= 0.537 \end{aligned}$$

so that the critical pressure is 0.537×62.0

$$= 33.30 \text{ lb./in.}^2 \text{ abs.}$$

The corrected value of T_B is now given by

$$T_B = 1600 \left(\frac{33 \cdot 30}{62 \cdot 0} \right)^{\frac{0 \cdot 351}{1 \cdot 351}} \\ = 1361 \cdot 4^\circ \text{ F. abs.}$$

The specific volume at the throat is given by

$$v_B = RT/144p = 53 \cdot 53 \times 1361 \cdot 4 / 144 \times 33 \cdot 30 \\ = 15 \cdot 20 \text{ ft.}^3 / \text{lb.}$$

In order to find the throat area, the throat velocity is required. This is found from the isentropic heat drop $(\Delta_s)_{AB}$ between A and B , i.e. between the temperatures $1600^\circ \text{ F. abs.}$ and $1361 \cdot 4^\circ \text{ F. abs.}$

Thus $(\Delta_s)_{AB}$

$$= 0 \cdot 21 (H_{1600} - H_{1361 \cdot 4})_{O_2} + 0 \cdot 79 (H_{1600} - H_{1361 \cdot 4})_{N_2} \\ = 0 \cdot 21 (11842 - 9909) + 0 \cdot 79 (11420 - 9622) \\ = 1827 \text{ B.Th.U./lb. mol.} = 63 \cdot 35 \text{ B.Th.U./lb.}$$

The velocity at the throat is given by

$$V_B = 223 \cdot 8 \sqrt{63 \cdot 35} \\ = 1781 \cdot 2 \text{ ft./sec.}$$

The throat area is now given by

$$A_B = 144 m v_B / V_B \\ = 144 \times 10 \times 15 \cdot 20 / 1781 \cdot 2 \\ = 12 \cdot 28 \text{ in.}^2$$

For the complete expansion through the nozzle it is necessary to find the isentropic heat drop from inlet to outlet. (This is determined in the same way as before when finding the throat area, but in this case the lower pressure is known, so that the entropy equation is, with T_D equal to the temperature at the nozzle outlet,

$$0 \cdot 21 \{ (S_{1600})_{O_2} - (S_{T_D})_{O_2} \} + 0 \cdot 79 \{ (S_{1600})_{N_2} - (S_{T_D})_{N_2} \} \\ = \frac{R}{J} \log_e 62 \cdot 0 / 14 \cdot 7$$

$$\text{or } 0 \cdot 21 (S_{1600})_{O_2} + 0 \cdot 79 (S_{1600})_{N_2} - \frac{R}{J} \log_e 62 \cdot 0 / 14 \cdot 7 \\ = 0 \cdot 21 (S_{T_D})_{O_2} + 0 \cdot 79 (S_{T_D})_{N_2} \dots \dots \dots (3)$$

The expression on the left of equation (3) is first determined, after which the temperature T_D is assumed and, if correct, it will be found that the equation is satisfied, otherwise the procedure is repeated until agreement is obtained.

Inserting the values $(S_{1600})_{O_2} = 57 \cdot 240$ and $(S_{1600})_{N_2} = 53 \cdot 617$, as given by the tables, on the left-hand side of equation (3) we have

$$0 \cdot 21 \times 57 \cdot 240 + 0 \cdot 79 \times 53 \cdot 617 - 1 \cdot 986 \times 2 \cdot 303 \log_e 62 \cdot 0 / 14 \cdot 7 \\ = 12 \cdot 021 + 42 \cdot 357 - 2 \cdot 859 \\ = 51 \cdot 52 \text{ E.U.}$$

If we assume $T_D = 1100^\circ \text{ F. abs.}$ the tables give $(S_{1100})_{O_2} = 54.260$ and $(S_{1100})_{N_2} = 50.842$ so that the right-hand side of equation (3) is then

$$\begin{aligned} 0.21 \times 54.260 + 0.79 \times 50.842 \\ = 51.56 \text{ E.U.} \end{aligned}$$

as against 51.52 E.U. for the left-hand side, so that the assumed value of $T_D = 1100^\circ \text{ F. abs.}$ may be accepted. The isentropic heat drop between $1600^\circ \text{ F. abs.}$ and $1100^\circ \text{ F. abs.}$ is now found from

$$\begin{aligned} (\Delta_s)_{AD} &= 0.21(H_{1600} - H_{1100})_{O_2} + 0.79(H_{1600} - H_{1100})_{N_2} \\ &= 0.21(11842 - 7855) + 0.79(11420 - 7704) \\ &= 3773 \text{ B.Th.U./lb. mol.} \end{aligned}$$

The net heat drop is 0.85 of $(\Delta_s)_{AD}$, so that we have

$$0.85 \times 3773 = 0.21(H_{1600} - H_{T_C})_{O_2} + 0.79(H_{1600} - H_{T_C})_{N_2} \dots\dots(4)$$

where T_C is the actual temperature at the nozzle outlet.

T_C has to be guessed so as to satisfy equation (4). Trying $T_C = 1200^\circ \text{ F. abs.}$ we have

$$\begin{aligned} 0.85 \times 3773 &= 0.21(11842 - 8631) + 0.79(11420 - 8430) \\ 3207 &= 3036, \end{aligned}$$

so that agreement is not obtained.

The heat drop calculated on the right-hand side of the equation is too low and therefore the guessed temperature is too high. By further trial and error it is found that the correct value of T_C is $1177^\circ \text{ F. abs.}$, so that the specific volume of the air at the nozzle exit is

$$\begin{aligned} v_c &= 53.53 \times 1177 / 144 \times 14.7 \\ &= 29.77 \text{ ft.}^3/\text{lb.} \end{aligned}$$

and the exit velocity is

$$\begin{aligned} V_C &= 223.8 \sqrt{111.2} \\ &= 2360 \text{ ft./sec.} \end{aligned}$$

since the net heat drop per pound of air is

$$3207 / 28.84 = 111.2 \text{ B.Th.U.}$$

The exit area is thus given by

$$\begin{aligned} A_C &= 144 \times 10 \times 29.77 / 2360 \\ &= 18.16 \text{ in.}^2 \end{aligned}$$

EXAMPLE 4

A closed vessel of 1 ft.^3 internal capacity contains air at a temperature of $4000^\circ \text{ F. abs.}$ and pressure of 1 atmosphere. If the air is cooled at constant volume to a temperature of $520^\circ \text{ F. abs.}$ which is the temperature of the surroundings and the heat thus liberated is used as a source

$$\begin{aligned}
 \text{The area } BCED &= 520(S_A - S_B) \\
 &= 520(0.02159 - 0.01758) \\
 &= 2.085 \text{ B.Th.U.}
 \end{aligned}$$

The change of internal energy ($E_A - E_B$) between A and B is given by

$$\begin{aligned}
 &n_{O_2}(E_A - E_B)_{O_2} + n_{N_2}(E_A - E_B)_{N_2} \\
 &= 0.0000719(24887 - 2574) + 0.0002707(23423 - 2581) \\
 &= 7.246 \text{ B.Th.U.}
 \end{aligned}$$

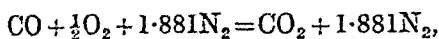
The available energy is thus

$$\begin{aligned}
 &7.246 - 2.085 \\
 &= 5.161 \text{ B.Th.U.}
 \end{aligned}$$

EXAMPLE 5

Calculation of maximum attainable temperature neglecting the formation of NO and assuming no dissociation of N_2 when CO is burned adiabatically at constant volume with the theoretical minimum air supply.

For this combustion, if carried to completion, the reaction equation is



assuming that the air consists of 21 per cent. of O_2 and 79 per cent. of N_2 by volume. Let the initial pressure, volume and temperature of the precombustion mixture be P_1 , V_1 and T_1 and the final corresponding values of the dissociated post-combustion mixture be P_2 , V_2 and T_2 with $V_2 = V_1$. Let the fractional volume of CO_2 dissociated be x mols per mol of CO_2 so that the amount of CO_2 remaining is $(1-x)$ mols. The oxygen liberated by the dissociation is $\frac{1}{2}x$ mols while the CO liberated is x mols. We thus have for the initial and final mixtures:

Initially at P_1 , V_1 and T_1					Finally at P_2 , V_2 and T_2				
CO	-	-	-	1 mol	CO	-	-	-	x mol
O_2	-	-	-	$\frac{1}{2}$ mol	CO_2	-	-	-	$(1-x)$ mol
N_2	-	-	-	1.881 mol	O_2	-	-	-	$\frac{1}{2}x$ mol
					N_2	-	-	-	1.881 mol
Total = 3.381 mol = m_1					Total = $(2.881 + \frac{1}{2}x)$ mol = m_2				

Let the partial pressures of the gases CO, CO_2 , O_2 and N_2 in the products of combustion be denoted by p_{CO} , p_{CO_2} , p_{O_2} and p_{N_2} . The ratio of these partial pressures of each gas to the total pressure P_2 of the mixture is the same as the ratio of the number of mols of

Since K_{pCO} is a function of T_2 there are two unknowns involved, namely T_2 and x . Another equation must therefore be established before these can be determined. This is given by the thermal energy equation which is established as follows.

The initial mixture of CO, O_2 and N_2 is considered as being heated at constant volume from T_1 to T_2 without change in composition. The heat required for this is the change in internal energy between T_1 and T_2 , that is,

$$(E_{CO} + \frac{1}{2}E_{O_2} + 1.881E_{N_2})_{T_2} - (E_{CO} + \frac{1}{2}E_{O_2} + 1.881E_{N_2})_{T_1}.$$

The CO is now allowed to burn at T_2 to CO_2 , liberating the heat of combustion H_{r_2} . The x mols of CO_2 are now dissociated for which the heat required is xH_{r_2} . If the complete process is adiabatic we have,

$$H_{r_2} - xH_{r_2} = (E_{CO} + \frac{1}{2}E_{O_2} + 1.881E_{N_2})_{T_2} - (E_{CO} + \frac{1}{2}E_{O_2} + 1.881E_{N_2})_{T_1} \dots (2)$$

An alternative way of regarding the process is as follows. The mol of CO is first burned completely to CO_2 at T_1 so that the heat liberated is H_{r_1} . The products now consist of 1 mol of CO_2 and 1.881 mol of N_2 . If these products are heated at constant volume to T_2 they absorb the heat

$$(E_{CO_2} + 1.881E_{N_2})_{T_2} - (E_{CO_2} + 1.881E_{N_2})_{T_1},$$

and finally, for the dissociation of x mols of CO_2 , the heat required is xH_{r_2} . For adiabatic conditions therefore

$$H_{r_1} - xH_{r_2} = (E_{CO_2} + 1.881E_{N_2})_{T_2} - (E_{CO_2} + 1.881E_{N_2})_{T_1} \dots (3)$$

This can be reduced to equation (2) but it is simpler to use it as it stands in solving for x with assumed T_2 values.

The above equations are now applied to the following particular case. One mol of CO along with the necessary air for theoretically correct combustion is contained in a closed space at a temperature of $600^\circ F$. abs. and pressure of 1 atmosphere. It is required to find the maximum attainable temperature due to adiabatic combustion of the CO at constant volume.

From the energy equation (3) we have with $H_{r_1} = 121198 \text{ B.Th.U./lb. mol}$ and

$$\begin{aligned} (E_{CO_2} + 1.881E_{N_2})_{600} &= (3434 + 1.881 \times 2979) \\ &= 9037 \text{ B.Th.U./lb. mol.} \end{aligned}$$

$$\text{Hence } 121198 - xH_{r_2} = (E_{CO_2} + 1.881E_{N_2})_{T_2} - 9037,$$

$$\text{or } xH_{r_2} = 130235 - (E_{CO_2} + 1.881E_{N_2})_{T_2} \dots (4)$$

By assuming values of T_2 the corresponding values of E_{CO_2} and E_{N_2} are found from the tables and x is then calculable from equation (4). Using these calculated values of x , the values of K_p are determined from equation (1) and plotted to a base of T_2 values. The true K_p values, as given by the tables, are also plotted to the same base. The point of intersection of the two curves gives the required upper temperature limit T_2 .

The work is conveniently arranged in tabular form as follows :

T_2	= 4800	4900	5000
E_{CO_2}	= 51606	52900	54197
$1.881E_{\text{N}_2}$	= 54229	55510	56793
$E_{\text{CO}_2} + 1.881E_{\text{N}_2}$	105835	108410	110990
	130235	130235	130235
xH_{v_2}	= 24400	21825	19245
H_{v_2}	= 113050	112813	112574
x	= 0.2158	0.1935	0.1710

At 4800° F. abs.

$$K_p = \frac{(1-x)}{x^2} \left(\frac{6.762 \times 600}{1 \times 4800} \right)^{\frac{1}{2}}$$

$$= \frac{0.7842}{0.2158^2} \left(\frac{4057.2}{4800} \right)^{\frac{1}{2}}$$

$$= 7.191$$

At 4900° F. abs.

$$K_p = \frac{0.8065}{0.1935^2} \left(\frac{6.762 \times 600}{1 \times 4900} \right)^{\frac{1}{2}}$$

$$= 8.624.$$

At 5000° F. abs.

$$K_p = \frac{0.8290}{0.1710^2} \left(\frac{6.762 \times 600}{1 \times 5000} \right)^{\frac{1}{2}}$$

$$= 10.565.$$

The curve AB (fig. 15) represents the true K_p values, while the curve CD represents the curve given by the K_p values calculated above.

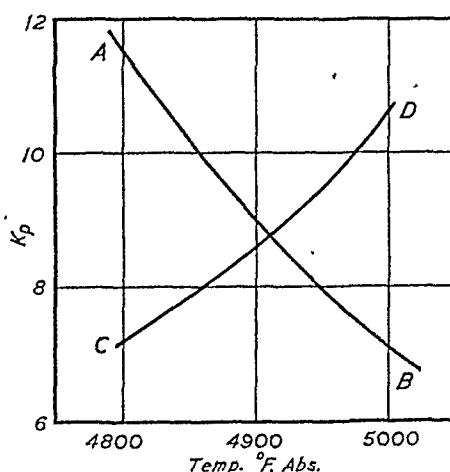


FIG. 15.

The curves intersect at $T_2 = 4908^\circ \text{F. abs.}$ which is therefore the maximum attainable temperature. The corresponding value of x , that

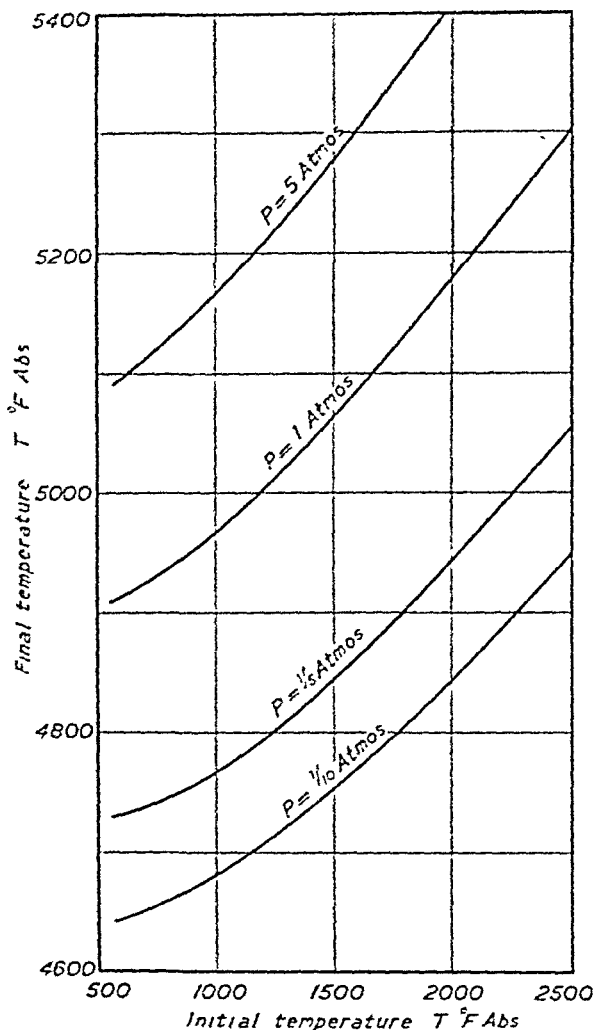


FIG. 16.

is the fractional amount of CO_2 dissociated, can now be found from the tabular calculation of equation (1) as follows :

T_2	=	4908
E_{CO_2}	=	53004
$1.881E_{\text{N}_2}$	=	55613
<hr/>		
$E_{\text{CO}_2} + 1.881E_{\text{N}_2}$	=	108617
		130235
<hr/>		
xH_{τ_1}	=	21618
H_{τ_1}		112832
x		0.1916

The percentage of CO_2 dissociated is thus 19.16.

The curves in fig. 16 show how the maximum attainable temperatures vary with different initial temperatures and different initial pressures, while those in fig. 17 show the percentage dissociation of CO_2 . The

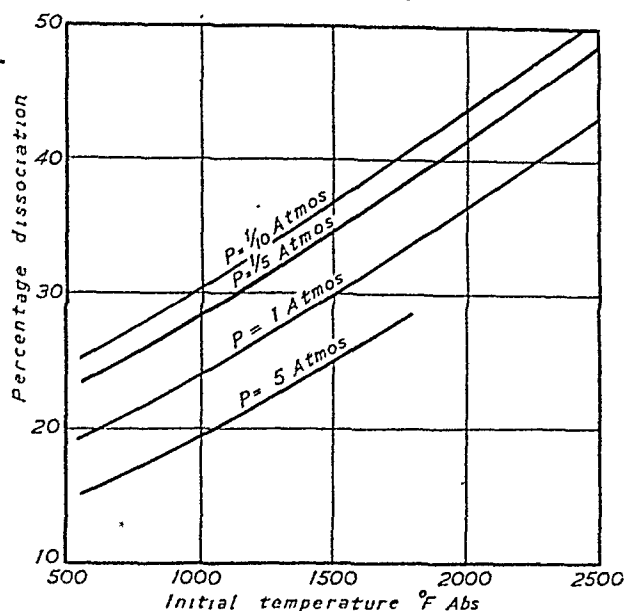


FIG. 17.

points required to plot these curves were obtained in the same way as shown in the sample calculation above, where the initial temperature was 600°F. abs. and the initial pressure was 1 atmosphere.

EXAMPLE 6

Calculation of Maximum Temperature in Gas Engine Cycle

The following data were obtained from a test carried out on a Crossley four-stroke gas engine in the James Watt Engineering Laboratories, The University of Glasgow.

Speed, 218 r.p.m.

Explosions, 100.5 per. min.

Temperature of exhaust gases, $1423^\circ \text{F. abs.}$

Gas consumption, 3.316 ft.³/min. at S.T.P.

Barometer, 29.37" Hg. or 14.42 lb./in.² abs.

Air consumption, 1.754 lb./min.

Stroke volume, 0.334 ft.³

Clearance volume, 0.092 ft.³

Pressure at beginning of suction stroke, 14.42 lb./in.² abs.

Pressure at end of suction stroke, 12.98 lb./in.² abs.

Also, assumed composition of air by volume : 79.1% N_2 , 20.9% O_2 ,
and by weight : 76.8% N_2 , 23.2% O_2 .

Molecular weight of air, 28.84.

From the above it is seen that the volume of air used per minute is

$$1.754 \times 359/28.84 = 21.83 \text{ ft.}^3 \text{ at S.T.P.}$$

Volume of air used per cycle is

$$21.83/109 = 0.2003 \text{ ft.}^3 \text{ at S.T.P.}$$

Volume of gas used per cycle is

$$3.316/100.5 = 0.0330 \text{ ft.}^3 \text{ at S.T.P.}$$

Air-gas ratio = $0.2003/0.0330 = 6.070$.

Volume of nitrogen in air supply per ft.³ of fuel gas is

$$0.791 \times 6.070 = 4.8014 \text{ ft.}^3$$

Volume of oxygen in air supply per ft.³ of fuel gas is

$$0.209 \times 6.070 = 1.2686 \text{ ft.}^3$$

For the determination of the ideal maximum gas temperature from the data found by experiment the following method has been adopted. The fuel gas analysis and air gas ratio enable the analysis of the post-combustion mixture to be obtained and this is assumed to be the same as that of the gases filling the clearance volume at the beginning of the suction stroke. Also the measured temperature of the gases leaving the engine is assumed to be the same as that of the gases filling the clearance volume at the beginning of suction so that the weight of these gases can be determined. The sum of the weights of the air, gas and residuals gives the total weight of the charge at the beginning of compression. The gas constant of the charge is found by calculation and hence the temperature at the beginning of compression can be determined.

The temperature T_2 at the end of isentropic compression is found by trial and error as follows. A tentative value of T_2 is first assumed and from this the absolute entropy of the charge is calculated. If this is found to be the same as the absolute entropy of the charge at the beginning of compression, i.e. at T_1 , the assumed value of T_2 is correct; otherwise a new value of T_2 is again assumed and the procedure is continued until the stated condition is satisfied.

In order to find T_3 , the temperature at the end of constant volume burning, the following method is adopted. From the calculated volumetric analysis of the charge the composition of the products with no dissociation is first determined and from this the composition of the products with dissociation is expressed in terms of x , y , u , and z , where

x = the number of mols of CO_2 dissociated to CO and O_2

y = the number of mols of H_2O dissociated to H_2 and O_2

u = the number of mols of H_2O dissociated to H_2 and OH .

z = the number of mols of NO formed from O_2 and N_2 .

The attainment of the final state of the constant volume burning period can be imagined as occurring in the following steps. The charge is

first burned isothermally and completely, i.e. without dissociation, at T_2 , the temperature at the end of compression. The products thus formed are then heated to an assumed equilibrium temperature T_3 after which they are dissociated, at this temperature, to give the final equilibrium state. The heat liberated by the combustion of the charge at T_2 must, under adiabatic conditions, be equal to that required to heat the products from T_2 to T_3 together with that required to effect the dissociation. An equation connecting x , y , u and z can thus be established. Since, however, there are five unknowns, namely, T_3 , x , y , u and z , four other equations are required for a complete solution. These are supplied by the equilibrium constants, $(K_p)_{H_2O}$, $(K_p)_{CO}$, $(K_p)_{OH}$ and $(K_p)_{NO}$. If the five equations are satisfied the assumed value of T_3 is correct, otherwise further trial and error is required until the conditions are satisfied.

The analysis of the Glasgow Corporation gas used in the test was as follows :

Gas	v	m	mv	w fractional
CO_2	0.033	44	1.452	0.1079
C_nH_m (assumed C_2H_4)	0.020	28	0.560	0.0416
O_2	0.009	32	0.288	0.0214
CO	0.152	28	4.256	0.3163
CH_4	0.180	16	2.880	0.2140
H_2	0.498	2	0.996	0.0740
N_2	0.108	28	3.024	0.2248
Apparent molecular weight, $\Sigma mv = 13.456$				1.0000

From this analysis of the fuel gas and the air gas ratio of 6.070, found above, the composition of the post-combustion mixture can now be found. This composition is assumed to be the same as that of the products which fill the clearance volume at the beginning of the suction stroke.

In fuel gas	Vol.	Vol. of CO_2 formed	Vol. of H_2O formed	Vol. of O_2 required
C_2H_4	0.020	0.040	0.040	0.060
CO	0.152	0.152	—	0.076
CH_4	0.180	0.180	0.360	0.360
H_2	0.498	—	0.498	0.249
CO_2	0.033	0.033	—	—
O_2	0.009	—	—	0.009
N_2	0.108	—	—	—
		$\Sigma CO_2 = 0.405$	$\Sigma H_2O = 0.898$	$\Sigma O_2 = 0.736$

The excess volume of oxygen in the products is

$$1.2686 - 0.7360 = 0.5326 \text{ ft.}^3$$

and the volume of nitrogen in the products is

$$4.8014 + 0.1080 = 4.9094 \text{ ft.}^3$$

The apparent molecular weight of the products is found tabularly as follows :

Gas	v per ft. ³ of gas	v fractional	m	mv
CO ₂	0.4050	0.0600	44	2.640
H ₂ O	0.8980	0.1331	18	2.396
O ₂	0.5326	0.0790	32	2.528
N ₂	4.9094	0.7279	28	20.381
	6.745	1.0000	$\Sigma mv = 27.945$	

The apparent molecular weight $= \frac{\Sigma mv}{v} = \frac{27.945}{1} = 27.95$ say. The universal gas constant $= 1546$ (with $R/J = 1.9869$). Hence the gas constant for the products is $1546/27.95 = 55.31 \frac{\text{ft. lb.}}{\text{lb.} \times ^\circ \text{F.}}$ and the weight of the residuals is given by

$$w_r = \frac{144 \times 14.42 \times 0.092}{55.31 \times 1423} = 0.002427 \text{ lb.}$$

The gas constant for the gaseous fuel is

$$R_g = 1546/13.46 = 114.9 \frac{\text{ft. lb.}}{\text{lb.} \times ^\circ \text{F.}}$$

so that the density of the gaseous fuel is

$$\rho_g = 144 \times 14.696/114.9 \times 492 = 0.0374 \text{ lb./ft.}^3 \text{ at S.T.P.}$$

The weight of gas supplied per working cycle is

$$w_g = v_g \rho_g$$

or

$$w_g = \frac{V_g \rho_g}{n}$$

where V_g is the volume of gas used per minute and n is the number of explosions per minute.

This gives

$$w_g = 3.316 \times 0.0374/100.5 = 0.001234 \text{ lb.}$$

The weight of air used per cycle is

$$w_a = \frac{W_a}{N/2} = 1.754/109 = 0.016092 \text{ lb.}$$

where W_a is the weight of air supplied per minute and N is the speed in revolutions per minute.

The total weight of the charge is thus

$$\begin{aligned} W &= w_r + w_a + w_o \\ &= 0.002427 + 0.016092 + 0.001234 \\ &= 0.019753 \text{ lb.} \end{aligned}$$

The gas constant for the charge is given by

$$\begin{aligned} R &= \frac{w_r R_r + w_o R_o + w_a R_a}{W} \\ &= \frac{0.002427 \times 53.31 + 0.001234 \times 114.9 + 0.016092 \times 53.58}{0.019753} \\ &= 57.62 \frac{\text{ft. lb.}}{\text{lb.} \times ^\circ \text{F.}} \end{aligned}$$

The temperature at the beginning of compression is given by

$$\begin{aligned} T_1 &= \frac{144 \times 12.98 \times 0.426}{0.019753 \times 57.62} \\ &= 699.5 \text{ or say} \\ &700^\circ \text{ F. abs.} \end{aligned}$$

The volume of the residuals at 14.42 lb./in.² abs. and 1423° F. abs. is 0.092 ft.³ so that the volume under S.T.P. conditions is

$$\begin{aligned} v_r' &= \frac{0.092 \times 492 \times 14.42}{14.696 \times 1423} \\ &= 0.0312 \text{ ft.}^3 \end{aligned}$$

The S.T.P. volume of fuel gas used per cycle is 0.0330 ft.³ (page 45) so that the volume of residuals per ft.³ of fuel gas is

$$0.0312/0.0330 = 0.9454 \text{ ft.}^3$$

The composition of the residuals is given on page 47 so that the volume of CO₂, H₂O, O₂ and N₂ in the residuals per ft.³ of fuel gas is found by multiplying each of the respective fractional volumes by 0.9454. This gives

$$\begin{array}{ll} \text{CO}_2 & 0.0600 \times 0.9454 = 0.0567 \\ \text{H}_2\text{O} & 0.1331 \times 0.9454 = 0.1258 \\ \text{O}_2 & 0.0790 \times 0.9454 = 0.0747 \\ \text{N}_2 & 0.7279 \times 0.9454 = 0.6882 \end{array}$$

Adding these to the total air and constituents of fuel gas the composition of the charge is as shown below :

	C ₂ H ₄	CO	CH ₄	H ₂	CO ₂	H ₂ O	O ₂	N ₂
Residuals	—	—	—	—	0.0567	0.1258	0.0747	0.6882
Air	—	—	—	—	—	—	1.2086	4.8014
Fuel gas	0.0200	0.1520	0.1800	0.4980	0.0330	—	0.0090	0.1080
Total	0.0200	0.1520	0.1800	0.4980	0.0897	0.1258	1.3523	5.5976
No. of mols per mol of charge	0.00250	0.01896	0.02246	0.06213	0.01119	0.01560	0.16871	0.69836

Pressure and Temperature of Charge at end of Compression

The composition of the charge given above enables the absolute entropy (S_1) to be determined at the beginning of compression and this must equal the absolute entropy (S_2) of the charge at the end of isentropic compression. Following the procedure indicated in example 2 we have (see equation 3. p. 30)

$$S_1 - S_2 = 0 = \Sigma m(S_T)_1 + \frac{R}{J} \log_e \frac{r_c}{T_1} - \Sigma m(S_T)_2 + \frac{R}{J} \log_e T_2 \dots\dots(1)$$

where r_c is the compression ratio. The first two terms on the right-hand side of the equation have a constant value and are therefore determined before proceeding with the subsequent trial and error calculation. Arranging the work in tabular form gives (with $T_1 = 700^\circ \text{F. abs.}$)

	$m(S_T)_1$
(for C_2H_4)	$0.00250 \times 56.466 = 0.14117$
(for CO)	$0.01896 \times 49.182 = 0.93249$
(for CH_4)	$0.02246 \times 46.826 = 1.05171$
(for H_2)	$0.06213 \times 33.078 = 2.05513$
(for CO_2)	$0.01119 \times 53.569 = 0.59944$
(for H_2O)	$0.01569 \times 47.285 = 0.74137$
(for O_2)	$0.16871 \times 50.913 = 8.58953$
(for N_2)	$0.69836 \times 47.648 = 33.27546$
	$\Sigma m(S_T)_1$
	<u>47.38630</u>

The second term in equation (1) is

$$\begin{aligned} \frac{R}{J} \log_e \frac{r_c}{T_1} &= -1.9869 \times 2.303 \log \frac{700}{4.631} \\ &= -9.97088 \end{aligned}$$

From previous trial and error methods it is found that with $T_2 = 1235^\circ \text{F. abs.}$ equation (1) is satisfied. This is confirmed as follows. The value of the last term in equation (1) is now given by

$$\begin{aligned} \frac{R}{J} \log_e T_2 &= 1.9869 \times 2.30258 \log 1235 \\ &= 14.1444. \end{aligned}$$

The value of $m(S_T)_2$ is conveniently found tabularly as follows :

	$m(S_T)_2$
(for C_2H_4)	$0.00250 \times 65.697 = 0.16424$
(for CO)	$0.01896 \times 53.240 = 1.00943$
(for CH_4)	$0.02246 \times 53.267 = 1.19638$
(for H_2)	$0.06213 \times 37.039 = 2.30123$
(for CO_2)	$0.01119 \times 59.687 = 0.66790$
(for H_2O)	$0.01569 \times 52.098 = 0.81742$
(for O_2)	$0.16871 \times 55.156 = 9.30537$
(for N_2)	$0.69836 \times 51.680 = 36.09124$
	<u>51.55321</u>

These calculated values, when inserted in equation (1), give

$$S_1 - S_2 = 47.38630 - 9.97088 - 51.5532 + 14.1444 \\ = 0.00661 \text{ E.U.}$$

which is near enough zero to justify the assumed value of $1235^\circ \text{ F. abs.}$ for T_2 . The corresponding pressure is found from

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

or

$$p_2 = \frac{p_1 V_1 T_2}{V_2 T_1} \\ = \frac{12.98 \times 4.631 \times 1235}{1 \times 700} \\ = 106.1 \text{ lb./in.}^2 \text{ abs.} \\ \text{or } 7.220 \text{ atmospheres.}$$

The composition of the charge is given on page 48, but the composition of the products formed with complete combustion is required. This is conveniently found from the following table.

	Mols produced		Mols of O_2 required	N_2
	CO_2	H_2O		
Combustion of—				
0.00250 mols of C_2H_4	0.00500	0.00500	0.00750	
0.01896 mols of CO	0.01896	—	0.00948	
0.02246 mols of CH_4	0.02246	0.04492	0.04492	
0.06213 mols of H_2	—	0.06213	0.03107	
Total	0.04642	0.11205	0.09297	
CO_2 present in charge	0.01119			
H_2O present in charge		0.01569		
O_2 present in charge			0.16871	
N_2 present in charge				0.69836
Total in products	0.05761	0.12774	0.07574	0.69836

The composition of the products with complete combustion is thus

$$\left. \begin{array}{ll} \text{CO}_2 & 0.05761 \\ \text{H}_2\text{O} & 0.12774 \\ \text{O}_2 & 0.07574 \\ \text{N}_2 & 0.69836 \end{array} \right\} \text{ per mol of charge.}$$

$$0.95945$$

Constant Volume Burning

Proceeding now along the lines indicated on p. 45 the heat of combustion of one mol of the charge at $T_2 = 1235^\circ \text{ F. abs.}$ and at constant volume, is first required. This is given by

$$\begin{aligned}
 H_r &= \Sigma m H_r \\
 &= 0.00250 \times 569916 + 0.01896 \times 120714 + 0.02246 \times 343952 \\
 &\quad + 0.06213 \times 104359 \\
 &= 17922.4 \text{ B.Th.U./lb. mol.}
 \end{aligned}$$

The products, the analysis of which is given on p. 50, are now heated at constant volume from $T_2 = 1235^\circ \text{ F. abs.}$ to the unknown final temperature T_3 which has at first to be assumed tentatively. The heat required for this is

$$\begin{aligned}
 &\Sigma m (E_{T_3} - E_{1235}) \\
 &= [0.05761 E_{\text{CO}_2} + 0.12774 E_{\text{H}_2\text{O}} + 0.07574 E_{\text{O}_2} + 0.69836 E_{\text{N}_2}]_{T_3} \\
 &\quad - 0.05761 \times 8941 - 0.12774 \times 7733 - 0.07574 \times 6453 - 0.69836 \times 6234 \\
 &= [0.05761 E_{\text{CO}_2} + 0.12774 E_{\text{H}_2\text{O}} + 0.07574 E_{\text{O}_2} + 0.69836 E_{\text{N}_2}]_{T_3} - 6345.
 \end{aligned}$$

If the products are now dissociated the heat required is

$$[x H_{\text{rCO}} + y H_{\text{rH}_2} + u H_{\text{rOH}} + z H_{\text{rNO}}]_{T_3}.$$

We thus have

$$\begin{aligned}
 17922 &= [0.05761 E_{\text{CO}_2} + 0.12774 E_{\text{H}_2\text{O}} + 0.07574 E_{\text{O}_2} + 0.69836 E_{\text{N}_2}]_{T_3} \\
 &\quad - 6345 + [x H_{\text{rCO}} + y H_{\text{rH}_2} + u H_{\text{rOH}} + z H_{\text{rNO}}]_{T_3}.
 \end{aligned}$$

This gives

$$\begin{aligned}
 &[x H_{\text{rCO}} + y H_{\text{rH}_2} + u H_{\text{rOH}} + z H_{\text{rNO}}]_{T_3} \\
 &= 24267 - [0.05761 E_{\text{CO}_2} + 0.12774 E_{\text{H}_2\text{O}} + 0.07574 E_{\text{O}_2} + 0.69836 E_{\text{N}_2}]_{T_3} \quad (1)
 \end{aligned}$$

From several trials it has been found that equation (1) along with the equilibrium constants is satisfied when $T_3 = 3872^\circ \text{ F. abs.}$ (T_3 is found by the method explained on p. 45.) This is confirmed as follows.

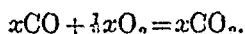
At $T_3 = 3872^\circ \text{ F. abs.}$ equation (1) becomes

$$\begin{aligned}
 &24267 - [115236x + 104378y + 121041u + 38827z] \\
 &= 24267 - [0.05761 \times 39747 + 0.12774 \times 31376 + 0.07574 \times 23974 \\
 &\quad + 0.69836 \times 22567] \\
 &= 24267 - 23889 \\
 &= 393,
 \end{aligned}$$

which gives

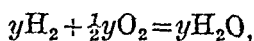
$$z = 0.010122 - 2.967934x - 2.688284y - 3.117444u. \dots\dots\dots (2)$$

As explained on p. 45, τ denotes the number of mols of CO_2 dissociated in accordance with the reaction equation

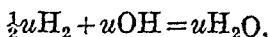


Hence the numbers of mols of CO and O_2 formed, due to this reaction, are x and $\frac{1}{2}x$ respectively while the number of mols of CO_2 is reduced

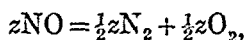
by x , giving $(0.05761 - x)$ mols. Similarly, due to the dissociation of y mols of H_2O in accordance with the reaction equation



we have y mols of H_2 and $\frac{1}{2}y$ mols of O_2 formed, leaving $(0.12774 - y)$ mols of H_2O . Due to the dissociation of u mols of H_2O in accordance with the reaction equation



we have $\frac{1}{2}u$ mols of H_2 and u mols of OH formed, leaving $(0.12774 - y - u)$ mols of H_2O . Finally, due to the formation of z mols of NO in accordance with the reaction equation



we have z mols of NO formed while the N_2 and O_2 are each reduced by $\frac{1}{2}z$ mols.

The composition of the post-combustion dissociated mixture at position 3 and T_3 is thus as follows :

Gas	No. of mols
CO	x
CO_2	$0.05761 - x$
H_2O	$0.12774 - u - y$
H_2	$0.12774 - y + 0.5u$
OH	u
O_2	$0.07574 + 0.5x + 0.5y - 0.5z$
NO	z
N_2	$0.69836 - 0.5z$
Total mols	$m_3 = 0.95936 + 0.5x + 0.5y + 0.5u$

The number of mols in the precombustion mixture is $m_2 = 1$.

The partial pressures of the gases in the dissociated state are expressed by the following relationships :

$$\frac{p_{CO_2}}{P_3} = \frac{0.05761 - x}{m_3},$$

but $P_2 V_2 = m_2 R T_2$

and $P_3 V_3 = m_3 R T_3$,

so that

$$\frac{P_2}{P_3} = \frac{m_2 T_2}{m_3 T_3},$$

or

$$\frac{P_3}{m_3} = \frac{P_2 T_3}{m_2 T_2}.$$

Hence,

$$p_{CO_2} = (0.05761 - x) \frac{P_2 T_3}{m_2 T_2}.$$

Similarly,

$$p_{\text{CO}} = \frac{P_2 T_3 x}{m_2 T_2},$$

$$p_{\text{H}_2\text{O}} = \frac{(0.12774 - u - y) P_2 T_3}{m_2 T_2},$$

$$p_{\text{H}_2} = \frac{(y + 0.5u) P_2 T_3}{m_2 T_2},$$

$$p_{\text{OH}} = \frac{P_2 T_3 u}{m_2 T_2},$$

$$p_{\text{O}_2} = \frac{(0.07574 + 0.5x + 0.5y - 0.5z) P_2 T_3}{m_2 T_2},$$

$$p_{\text{NO}} = \frac{P_2 T_3 z}{m_2 T_2},$$

$$p_{\text{N}_2} = \frac{(0.69836 - 0.5z) P_2 T_3}{m_2 T_2}.$$

The equilibrium constants are given by the following expressions :

$$K_{p_{\text{CO}_2}} = \frac{p_{\text{CO}_2}}{p_{\text{CO}} \cdot p_{\text{O}_2}^{\frac{1}{2}}}$$

$$= \frac{(0.05761 - x)}{x(0.07574 + 0.5x + 0.5y - 0.5z)^{\frac{1}{2}}} \left(\frac{m_2 T_2}{P_2 T_3} \right)^{\frac{1}{2}},$$

but $m_2 = 1$; $T_2 = 1235^\circ \text{ F. abs.}$; $P_2 = 7.220 \text{ atm.}$, giving

$$K_{p_{\text{CO}_2}} = \frac{13.079(0.05761 - x)}{x(0.07574 + 0.5x + 0.5y - 0.5z)^{\frac{1}{2}} T_3^{\frac{1}{2}}} \dots\dots\dots(3)$$

$$K_{p_{\text{w.g.}}} = \frac{p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}}{p_{\text{H}_2} \cdot p_{\text{CO}_2}}$$

$$= \frac{x(0.12774 - u - y)}{(0.05761 - x)(y + 0.5u)} \dots\dots\dots(4)$$

$$K_{p_{\text{OH}}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{OH}} \cdot p_{\text{H}_2}^{\frac{1}{2}}}$$

$$= \frac{13.079(0.12774 - u - y)}{u(y + 0.5u)^{\frac{1}{2}} T_3^{\frac{1}{2}}} \dots\dots\dots(5)$$

$$K_{p_{\text{NO}}} = \frac{p_{\text{NO}}}{p_{\text{N}_2}^{\frac{1}{2}} p_{\text{O}_2}^{\frac{1}{2}}}$$

$$= \frac{z}{(0.69836 - 0.5z)^{\frac{1}{2}} (0.07574 + 0.5x + 0.5y - 0.5z)^{\frac{1}{2}}} \dots\dots\dots(6)$$

Equations (2), (3), (4), (5) and (6) form the conditions of equilibrium and the method of solution is as follows. A probable value of T_3 is first guessed and, with $y = 0$, u is determined from equation (5). Substituting these values for u and y in equation (4) the value of x is determined.

Equation (2) can then be solved to give the value of z . Equation (3) must now be satisfied by the values of x , y and z as obtained above. If equation (3) is not satisfied another value for y must be assumed and the process repeated until equation (3) is satisfied. If these assumed values are correct equation (6) must also be satisfied. If not, the whole process is repeated with a new value for T_3 until all equations are satisfied simultaneously.

Solving the equations in the above manner gave $T_3 = 3872^\circ \text{ F. abs.}$ with $u = 0.001450$ and $y = -0.0006434$ as shown by equation (5). Thus with $K_{p_{\text{OH}}} = 2036$ at $T_3 = 3872^\circ \text{ F. abs.}$ we have, for the right-hand side of equation (5),

$$\frac{13.079(0.12774 - 0.001450 + 0.0006434)}{0.002565(0.000737 - 0.0006545)^{\frac{1}{2}} \times 62.225} = 2037,$$

so that the equation is satisfied.

Substituting these values in equation (4) gives

$$x = 0.00019594; (K_{p_{\text{w.g.}}})_{T_3=3872} = 5.3088.$$

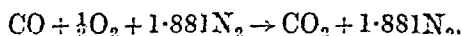
Equation (2) now gives

$$z = 0.006750.$$

If the assumed values of T_3 and u are correct, it will be found that the derived values of x , y and z satisfy equations (3) and (6).

Thus the right-hand side of equation (3) is 229.5 as against 221 given in the tables for $K_{p_{\text{CO}_2}}$ and the right-hand side of equation (6) is 0.03015 as against 0.02961 given in the tables for $K_{p_{\text{NO}_2}}$.

Hence the maximum attainable temperature is $3872^\circ \text{ F. abs.}$

Chemical Reaction

This gives, as the working substance, 1 mol of $\text{CO}_2 + 1.881$ mols of N_2 and it will be assumed that this mixture completely fills the cylinder at the beginning of compression, the pressure being one atmosphere and the temperature 600°F. abs.

Compression

$$P_1 = 1; V_1 = 5; T_1 = 600^\circ \text{F. abs.}$$

The total entropy for a mixture of gases at any pressure P and temperature T is given by

$$S = \Sigma(mS_T) + \Sigma m \frac{R}{J} \log_e \frac{\Sigma m}{m} - \Sigma m \frac{R}{J} \log_e P.$$

Hence at the beginning of compression the entropy, as shown in the following table, is 143.405.

Gases	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10} \frac{\Sigma m}{m}$	$4.575m \log_{10} \frac{\Sigma m}{m}$
CO_2	1	52.104	52.104	2.8810	0.45954	2.102
N_2	1.881	46.574	87.606	1.5316	0.18514	1.593
$\Sigma m = 2.881$;		$\Sigma(mS_T) = 139.710$;		$\Sigma \left(4.575m \log_{10} \frac{\Sigma m}{m} \right) = 3.695$		

$$S_{600} = 139.710 + 3.695 = 143.405 \text{ E.U.}$$

The pressure and temperature at the end of compression are found to be 8.4301 atmospheres and $1012^\circ \text{F. abs.}$ respectively, the entropy being 143.405 E.U.

Constant Volume Heating

The heat available for heating the CO_2 and N_2 will be taken as the heat of reaction at constant volume of one mol of CO at $1012^\circ \text{F. abs.}$ which according to the tables is 120990 B.Th.U. Using this value for the heat available the maximum temperature attainable in the cylinder may be determined and the amount of dissociation. Denoting the number of mols of CO_2 dissociated by x , the value of $K_{r\text{CO}_2}$ at any temperature T_3 is given by

$$K_{r\text{CO}_2} = \frac{(1-x)}{x(0.5x)^{\frac{1}{2}}} \left(\frac{m_2 T_2}{P_2 T_3} \right)^{\frac{1}{2}},$$

where the suffix 2 refers to conditions at the end of compression. See figure 18.

$m_2 = 2.881$; $T_2 = 1012^\circ \text{F. abs.}$ and $P_2 = 8.4301$ atmospheres, so that

$$K_{r\text{CO}_2} = \frac{18.597(1-x)}{x(0.5x)^{\frac{1}{2}}} \cdot \frac{1}{T_3^{\frac{1}{2}}} \dots\dots\dots(1)$$

The second equation required for the determination of T_3 and x is supplied by the energy relationship

$$H_{v_2} = [E_{\text{CO}_2} + 1.881E_{\text{N}_2}]_{T_2}^{T_3} + (xH_{v_1})_{\text{CO}} \dots\dots\dots(2)$$

where the suffix 3 refers to the point on the diagram at the end of constant volume combustion. T_2 is known so that equation (2) becomes

$$120990 = [E_{\text{CO}_2} + 1.881E_{\text{N}_2}]_{T_2} - 6832 - 9518 + (xH_{v_1})_{\text{CO}}$$

or

$$xH_{v_1} = 137340 - [E_{\text{CO}_2} + 1.881E_{\text{N}_2}]_{T_2} \dots\dots\dots(3)$$

By choosing a series of values for T_3 a corresponding set of values of x is found from equation (3) and the correct value of T_3 is obtained when the corresponding value of x satisfies equation (1). This is found to be the case when $T_3 = 5252^\circ \text{ F. abs.}$, giving for equation (3)

$$111977x = 137340 - 57473 - 60034,$$

from which

$$x = 0.1771.$$

Substituting $x = 0.1771$ in the right-hand side of equation (1) gives

$$K_{\text{CO}_2} = 4.0070,$$

which is very close to the tabulated value at $5252^\circ \text{ F. abs.}$

So far the calculation has given the compression line and the temperature attained at the end of constant volume heating, but the shape of the curve representing combustion has still to be determined. If the heating of the CO_2 and N_2 proceeds to completion through a series of equilibrium state points equation (1) must give the relation between x and T at any temperature T . With the composition of the gases fixed at each temperature the entropy may be calculated for the corresponding gaseous mixture and the state points plotted on a temperature-entropy diagram.

The following table gives the values of x for a series of temperatures from $3000^\circ \text{ F. abs.}$, below which x is insignificant, to $5252^\circ \text{ F. abs.}$, the maximum temperature reached, together with the total entropy at the same temperatures.

$T^\circ \text{ F. abs.}$	x	S
3000	0.000808	167.015 (taking $x=0$)
3500	0.0052	171.003
4000	0.0205	174.814
4500	0.0582	178.801
5000	0.1286	183.154
5252	0.1771	185.467

The details of the calculation are shown below for $T_3 = 5252^\circ \text{ F. abs.}$

Gas	m	ST	mST	$\frac{\Sigma m}{m}$	$\log_{10} \frac{\Sigma m}{m}$	$4.575m \log_{10} \frac{\Sigma m}{m}$
CO	0.17710	65.233	11.553	16.7680	1.22449	0.992
CO ₂	0.82290	79.530	65.445	3.6086	0.55732	2.098
O ₂	0.08855	67.728	5.997	33.5350	1.52550	0.618
N ₂	1.88100	63.546	119.530	1.5787	0.19830	1.706

$$\Sigma m = 2.96955; \quad \Sigma(mST) = 202.525; \quad \Sigma(4.575m \log_{10} \frac{\Sigma m}{m}) = 5.414$$

$$P_3 = \frac{8.4301 \times 2.96955 \times 5252}{2.881 \times 1012}$$

$$= 45.095 \text{ atmospheres.}$$

$$S \text{ at } 5252^\circ \text{ F. abs.} = 202.525 + 5.414 - 2.96955 \times 4.575 \log_{10} 45.095$$

$$= 185.467 \text{ E.U.}$$

The state points between $1012^\circ \text{ F. abs.}$ and $3000^\circ \text{ F. abs.}$ are the same as those obtained when no dissociation occurs and may be obtained from the table given on page 59. The temperature T_4 at the end of isentropic expansion is given by the point of intersection of the constant volume curve through 1 and the perpendicular through the point 3.

Constant Volume Curve 1-4

The location of points on this curve is similar to that outlined above for the curve 2-3. The equilibrium constant at any temperature T is given by the expression

$$K_{p_{\text{CO}_2}} = \frac{(1-x)}{x(0.5x)^{\frac{1}{2}}} \left(\frac{m_1 T_1}{P_1 T} \right)^{\frac{1}{2}} \dots\dots\dots (4)$$

where the suffix 1 refers to the point at the beginning of compression with $m_1 = 2.881$, $T_1 = 600^\circ \text{ F. abs.}$ and $P_1 = 1$ atmosphere.

Substituting these values in equation (4) gives

$$K_{p_{\text{CO}_2}} = \frac{41.576(1-x)}{x(0.5x)^{\frac{1}{2}} T^{\frac{1}{2}}} \dots\dots\dots (5)$$

For any value of T , $K_{p_{\text{CO}_2}}$ is fixed so that x can be determined. The total entropy of the mixture is then calculable. The following table gives the values of x for a series of temperatures from $2500^\circ \text{ F. abs.}$ where x is taken as zero to $4125^\circ \text{ F. abs.}$ where it will be found that the vertical from the point 3 cuts the constant volume curve.

$T^\circ \text{ F. abs.}$	x	S
2500	0	171.851
3000	0.00138	176.285
3500	0.00886	180.344
4000	0.03478	184.477
4125	0.04606	185.571

The calculation for S at $4125^\circ \text{ F. abs.}$ is given below and it will

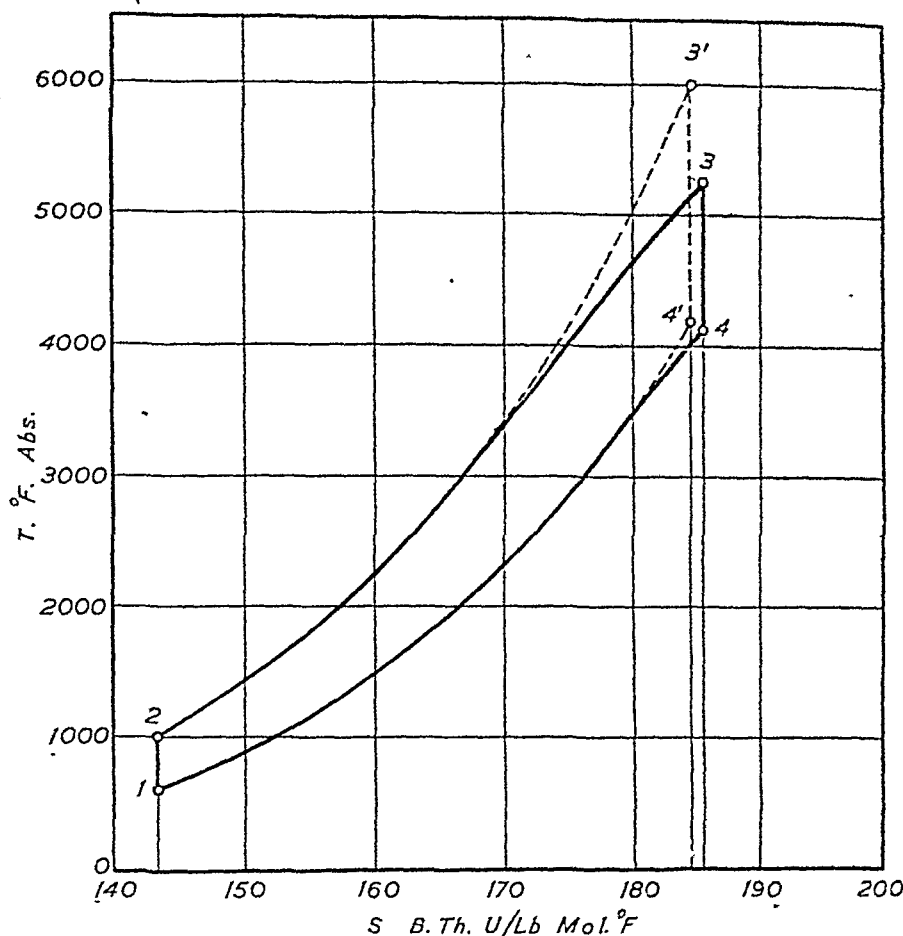


FIG. 18.

be seen that the value obtained is not appreciably different from 185.467 E.U.

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10} \frac{\Sigma m}{m}$	$4.575m \log_{10} \frac{\Sigma m}{m}$
CO	0.04606	63.102	2.906	63.049	1.79967	0.379
CO ₂	0.95394	75.947	72.449	3.0412	0.48347	2.110
O ₂	0.02303	65.474	1.508	126.10	2.10071	0.221
N ₂	1.88100	61.426	115.542	1.5439	0.18892	1.626

$$\Sigma m = \underline{2.90403}; \quad \Sigma mS_T = \underline{192.405}; \quad \Sigma \left(4.575m \log_{10} \frac{\Sigma m}{m} \right) = \underline{4.336}$$

$$P_4 = \frac{1 \times 2.90403 \times 4125}{2.881 \times 600}$$

$$= 6.930 \text{ atmos.}$$

$$S \text{ at } 4125^\circ \text{ F. abs.} = 192.405 + 4.336 - 11.170$$

$$= 185.571 \text{ E.U.}$$

The state points between 600° F. abs. and 2500° F. abs. inclusive may be obtained from the table on page 60 for the undissociated gas mixture. The cycle, taking into account the dissociation of CO₂ and

neglecting the formation of NO, can now be drawn on the temperature-entropy diagram. To show the effect dissociation has on the cycle it is convenient at this stage to plot the cycle, when dissociation is neglected, on the same diagram as that in which dissociation is taken into account.

Ideal Cycle without Dissociation

Compression. The compression curve is the same as that in the cycle in which dissociation is taken into account.

Heat Reception at Constant Volume

Before calculating the entropies for a series of temperatures the maximum temperature which can be reached should be calculated. The heat available for increasing the internal energy of the CO_2 and N_2 will be the lower heat of reaction at constant volume, H_{r_v} , which, as previously determined, is 120990 B.Th.U./lb. mol. This heat goes to increase the internal energy of the CO_2 and N_2 while satisfying the following thermal relation.

$$120990 = [E_{\text{CO}_2} + 1.881E_{\text{N}_2}]_{T_2'}^{T_1'} \dots\dots\dots (6)$$

$T_2 = 1012^\circ \text{ F. abs.}$ and equation (6) becomes

$$120990 = [E_{\text{CO}_2} + 1.881E_{\text{N}_2}]_{T_2'} - 6832 - 9518$$

or

$$137340 = [E_{\text{CO}_2} + 1.881E_{\text{N}_2}]_{T_2'} \dots\dots\dots (7)$$

Equation (7) is approximately solved with $T_2' = 6015^\circ \text{ F. abs.}$ which gives the right-hand side as $67441 + 69919 = 137360$ as against 137340 for the left-hand side.

Using the general expression for the entropy the following table may be drawn up for the curve of constant volume heating, the pressures in atmospheres being given along with the entropy at temperatures from $2000^\circ \text{ F. abs.}$ to $6015^\circ \text{ F. abs.}$

$T^\circ \text{ F. abs.}$	$P \text{ (atmos.)}$	S
2000	16.660	157.485
2500	20.825	162.638
3000	24.990	167.015
3500	29.155	170.813
4000	33.321	174.170
4500	37.486	177.153
5000	41.651	179.855
5500	45.816	182.323
6015	50.106	184.655

The calculation for the entropy and pressure is given below for 6015° F. abs.

$$P_3 = \frac{6015}{1012} \times 8.4301 = 50.106 \text{ atmospheres.}$$

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10} \frac{\Sigma m}{m}$	$4.575m \log_{10} \frac{\Sigma m}{m}$
CO ₂	1	81.571	81.571	2.8810	0.45954	2.102
N ₂	1.881	64.750	121.795	1.5316	0.18514	1.503
$\Sigma m = 2.881$;		$\Sigma(mS_T) = 203.366$;		$\Sigma \left(4.575m \log_{10} \frac{\Sigma m}{m} \right) = 3.695$		

S at 6015° F. abs.

$$= 203.366 + 3.695 - 2.881 \times 4.575 \log_{10} 50.106$$

$$= 184.655 \text{ E.U.}$$

As before the temperature at the end of expansion is found by dropping a vertical from 3' to cut the constant volume curve through 1. This curve lies to the right of the curve 2-3', the horizontal intercepts being equal between the curves. This intercept is

$$m_1 \frac{R}{J} \log_e 5 = 2.881 \times 4.575 \log_{10} 5 = 9.213.$$

If this amount is added to the table of entropies on p. 59, the following values are obtained for temperatures from 2000° F. abs. to 4190° F. abs. at which temperature level the vertical from 3' meets the curve.

T	S
2000	166.698
2500	171.851
3000	176.228
3500	180.026
4000	183.383
4190	184.566.

The following table gives the details of the calculation with $T = 4190^\circ \text{ F. abs.}$

$$P_4 = \frac{4190}{600} = 6.9835 \text{ atmos.}$$

Gas	m	S_T	mS_T
CO ₂	1	76.178	76.178
N ₂	1.881	61.562	115.798
$\Sigma m = 2.881$		$\Sigma(mS_T) = 191.976$	

$$\Sigma \left(4.575m \log_{10} \frac{\Sigma m}{m} \right) = 3.695 \text{ as before.}$$

Hence,

S at 4190° F. abs.

$$= 191.976 + 3.695 - 2.881 \times 4.575 \log_{10} 6.9835$$

$$= 191.976 + 3.695 - 11.125$$

$$= 184.546 \text{ (as against } 184.655).$$

*Ideal Thermal Efficiency**(a) Cycle with Dissociation*

The heat supplied is the area under the curve 2-3, i.e. H_r at 1012° F. abs. or 120990 B.Th.U. The heat rejected is the area under the curve 4-1, i.e. 84268 B.Th.U.

Hence the efficiency is

$$\begin{aligned}\eta &= \frac{\text{Heat supplied} - \text{Heat rejected}}{\text{Heat supplied}} \\ &= \frac{120990 - 84268}{120990} \\ &= 0.3035 \text{ or } 30.35\%.\end{aligned}$$

(b) Cycle without Dissociation

In this case the efficiency is given by

$$\eta = \frac{(E_3 - E_2) - (E_4 - E_1)}{(E_3 - E_2)}$$

but $E_3 - E_2 = H_{r_2} = 120990$ and $E_4 - E_1$ is the difference in internal energy of the products between the temperatures 4190° F. abs. and 600° F. abs., i.e.

$$\begin{aligned}E_4 - E_1 &= \sum m E_{4190} - \sum m E_{600} \\ &= (43784 + 46461) - (3434 + 5603) \\ &= 81208.\end{aligned}$$

Hence the value of the efficiency is given by

$$\begin{aligned}\eta &= \frac{120990 - 81208}{120990} \\ &= 0.3288 \text{ or } 32.88\%.\end{aligned}$$

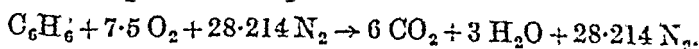
The error in neglecting dissociation is thus about 8.3 per cent.

EXAMPLE 9. *Ideal attainable Efficiency of the Constant Volume Cycle using the Products from the Combustion of Benzene as the Working Substance*

Only the main results need be indicated here as the method of solution is similar to that of example 8. It is assumed that the working substance throughout the cycle consists of the products formed by the combustion of one mol of benzene with the theoretically correct air. The temperature and pressure at the beginning of compression are taken as 600° F. abs. and 1 atmosphere. The ideal cycle consists of (fig. 19):

- (a) Isentropic compression with a compression ratio of 5;
- (b) Heat reception at constant volume;
- (c) Isentropic expansion;
- (d) Heat rejection at constant volume.

The reaction equation is expressed as



(a) *Compression*

The absolute entropy at the beginning of compression is found tabularly as follows :

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10} \frac{\Sigma m}{m}$	$4.575m \log_{10} \frac{\Sigma m}{m}$
CO_2	6.000	52.104	312.624	6.2023	0.79255	21.755
H_2O	3.000	46.034	138.102	12.405	1.09360	15.010
N_2	28.214	46.574	1314.039	1.3190	0.12022	15.518

$$\Sigma m = \underline{37.214}; \quad \Sigma(mS_T) = \underline{1764.765}; \quad \Sigma\left(4.575m \log_{10} \frac{\Sigma m}{m}\right) = \underline{52.283}$$

$$S_{600} = \Sigma(mS_T) + \Sigma\left(4.575m \log_{10} \frac{\Sigma m}{m}\right) \\ = 1817.048 \text{ E.U.}$$

The pressure P_2 at the end of compression is found from the relationship

$$P_2 V_2 / T_2 = P_1 V_1 / T_1$$

giving

$$P_2 = 1 \times 5 \times T_2 / 600 \\ = T_2 / 120.$$

By trial and error it is found that $T_2 = 1057^\circ \text{F. abs.}$ satisfies the condition of equal absolute entropies at the points 1 and 2. Thus, tabulating, we have

Gas	m	S_T	mS_T
CO_2	6.000	57.893	347.358
H_2O	3.000	50.727	152.181
N_2	28.214	50.548	1426.161
		$\Sigma(mS_T) = \underline{1925.700}$	

$$P_2 = 1057/120 \\ = 8.8083 \text{ atm.}$$

and

$$\Sigma m 4.575 \log_{10} P_2 / P_1 \\ = 37.214 \times 4.575 \times 0.94489 \\ 160.871 \text{ E.U.}$$

Hence

$$S_{1057} = 1925.700 + 52.283 - 160.871 \\ = 1817.112 \text{ E.U.}$$

as against 1817.048 E.U. at the beginning of compression.

(b) *Heating at constant volume*

The énergy equation is given by

$$H_{T_2} = [6E_{\text{CO}_2} + 3E_{\text{H}_2\text{O}} + 28.214E_{\text{N}_2}]_{T_2} + [xH_{\text{vCO}} + yH_{\text{H}_2\text{O}} + uH_{\text{vOH}} + zH_{\text{vNO}}]_{T_2},$$

where H_{T_1} is the heat of reaction of benzene at T_2 , i.e. 1362140 B.Th.U./lb. mol and since the internal energies of 6 mols of CO_2 ,

of 3 mols of H_2O and 28.214 mols of N_2 are respectively 43464, 19548 and 149365 at $T_2 = 1057^\circ$ F. abs., the energy equation becomes

$$1362140 = [6E_{CO_2} + 3E_{H_2O} + 28.214E_{N_2}]_{T_2} - 43464 - 19548 - 149365 \\ + [xH_{rCO} + yH_{rH_2} + uH_{rOH} + zH_{rNO}]_T$$

or

$$[xH_{rCO} + yH_{rH_2} + uH_{rOH} + zH_{rNO}]_{T_2} \\ = 1574517 - [6E_{CO_2} + 3E_{H_2O} + 28.214E_{N_2}]_{T_2}$$

The equilibrium equations are

$$K_{rCO_2} = \frac{6-x}{x(0.5x+0.5y-0.5z)^{\frac{1}{2}}} \left(\frac{m_2 T_2}{P_2 T_3} \right)^{\frac{1}{2}},$$

$$K_{rH_2O} = \frac{(3-u-y)x}{(6-x)(y+0.5u)},$$

$$K_{rOH} = \frac{3-u-y}{u(y+0.5u)^{\frac{1}{2}}} \left(\frac{m_2 T_2}{P_2 T_3} \right)^{\frac{1}{2}},$$

$$K_{rNO} = \frac{z}{(28.214-0.5z)^{\frac{1}{2}}(0.5x+0.5y-0.5z)^{\frac{1}{2}}},$$

and with $T_2 = 1057^\circ$ F. abs., $P_2 = 8.8083$ atmospheres and $m_2 = 37.214$ mols, these equations become

$$K_{rCO_2} = \frac{66.827(6-x)}{x(0.5x+0.5y-0.5z)^{\frac{1}{2}}} \cdot \frac{1}{T_3^{\frac{1}{2}}} \dots\dots\dots I$$

$$K_{rH_2O} = \frac{(3-u-y)x}{(6-x)(y+0.5u)} \dots\dots\dots II$$

$$K_{rOH} = \frac{66.827(3-u-y)}{u(y+0.5u)^{\frac{1}{2}}} \cdot \frac{1}{T_3^{\frac{1}{2}}} \dots\dots\dots III$$

$$K_{rNO} = \frac{z}{(28.214-0.5z)^{\frac{1}{2}}(0.5x+0.5y-0.5z)^{\frac{1}{2}}} \dots\dots\dots IV$$

By trial and error it is found that the above equations are all satisfied at $T_3 = 5215^\circ$ F. abs. Thus at this temperature the values of $6E_{CO_2}$, $3E_{H_2O}$ and $28.214E_{N_2}$ are 341946, 138231 and 893340, so that the right-hand side of the energy equation given on p. 62 is equal to

$$1574517 - (341946 + 138231 + 893340) \\ = 201000 \text{ B.Th.U.}$$

The corresponding values of H_{rCO} , H_{rH_2} , H_{rOH} and H_{rNO} are 112065, 103386, 119673 and 38647. The energy equation thus becomes

$$112065x + 103386y + 119673u + 38647z = 201000,$$

so that

$$z = 5.200915 - 2.899704x - 2.675133y - 3.096563u.$$

The equilibrium constants at $T_3 = 5215^\circ \text{ F. abs.}$ are

$$K_{p\text{CO}_2} = 4.2806; K_{p\text{w.g.}} = 7.4166; K_{p\text{OH}} = 31.146; K_{p\text{NO}} = 0.10818,$$

so that

$$4.2806 =$$

$$\frac{66.827 (6-x)}{x(0.5x + 0.5y - 2.600457 + 1.449852x + 1.337567y + 1.548282u)^{\frac{1}{2}} \times 72.215}$$

giving

$$4.6257 = \frac{(6-x)}{x(1.949852x + 1.837567y + 1.548282u - 2.600457)^{\frac{1}{2}}} \dots\dots\dots \text{I (a)}$$

$$7.4166 = \frac{(3-u-y)x}{(6-x)((y+0.5u))} \dots\dots\dots \text{II (a)}$$

$$31.146 = \frac{66.827(3-u-y)}{u(y+0.5u)^{\frac{1}{2}} 72.215}$$

giving

$$33.657 = \frac{3-u-y}{u(y+0.5u)^{\frac{1}{2}}} \dots\dots\dots \text{III (a)}$$

$$0.10818 = \frac{z}{(28.214 - 0.5z)^{\frac{1}{2}} (0.5x + 0.5y - 0.5z)^{\frac{1}{2}}} \dots\dots\dots \text{IV (a)}$$

With a finally assumed value of $u = 0.2437$ equation III (a) gives $y = -0.00823$,

so that

$$7.4166 = \frac{2.76453x}{(6-x)0.11362}$$

from which $x = 1.40165$.

The right-hand side of equation I (a) then equals 4.6641 as against 4.6257 on the left-hand side. Accepting these values therefore for x , y and u and inserting them in the energy equation gives

$$\begin{aligned} z &= 5.20092 - 4.06437 + 0.02202 - 0.75463 \\ &= 0.40394. \end{aligned}$$

The right-hand side of equation IV (a) then becomes

$$\frac{0.40394}{5.2926 \times 0.70339} = 0.10851$$

as against 0.10818 on the left-hand side so that the assumed values may be accepted.

The table below, which is drawn up for the purpose of calculating the entropy of the products at the end of the constant volume burning period, i.e. at the point 3, also shows the composition of the dissociated products at that point.

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10} \frac{\Sigma m}{m}$	$4.575m \log_{10} \frac{\Sigma m}{m}$
CO ₂	4.59835	79.425	365.224	8.2709	0.91756	19.303
CO	1.40165	65.170	91.345	27.134	1.43350	9.192
H ₂ O	2.76453	68.061	188.157	13.757	1.13852	14.400
H ₂	0.11362	48.166	5.473	334.73	2.52470	1.312
OH	0.24370	61.091	14.888	156.06	2.19329	2.445
O ₂	0.49475	67.661	33.475	76.872	1.88577	4.268
NO	0.40394	68.563	27.695	94.154	1.97384	3.648
N ₂	28.01203	63.483	1778.288	1.3577	0.13276	17.014

$$\Sigma m = 38.03257; \quad \Sigma(mS_T) = 2504.545; \quad \Sigma(4.575m \log_{10} \frac{\Sigma m}{m}) = 71.582$$

$$P_3 = \frac{8.8083 \times 38.03257 \times 5215}{37.214 \times 1057}$$

$$= 44.414 \text{ atmospheres.}$$

$$S_{5215} = 2504.545 + 71.582 - 38.03257 \times 4.575 \log_{10} 44.414$$

$$= 2289.460 \text{ E.U.}$$

The state point at the end of constant volume burning can thus be located on the $T'S$ field but, in order to represent the constant volume combustion curve, it is necessary to determine the entropies of the equilibrium mixtures at various temperature levels. At any temperature T the equilibrium constants are expressed by the relationships:

$$K_{x\text{CO}_2} = \frac{66.827(6-x)}{x(0.5x+0.5y-0.5z)^{\frac{1}{2}}} \cdot \frac{1}{T^{\frac{1}{2}}} \dots\dots\dots \text{I}$$

$$K_{x\text{H}_2\text{O}} = \frac{(3-u-y)x}{(6-x)(y+0.5u)} \dots\dots\dots \text{II}$$

$$K_{x\text{OH}} = \frac{66.827(3-u-y)}{u(y+0.5u)^{\frac{1}{2}}} \cdot \frac{1}{T^{\frac{1}{2}}} \dots\dots\dots \text{III}$$

$$K_{x\text{NO}} = \frac{z}{(28.214-0.5z)^{\frac{1}{2}}(0.5x+0.5y-0.5z)^{\frac{1}{2}}} \dots\dots\dots \text{IV}$$

At 4500° F. abs. these become

$$26.303 = \frac{66.827(6-x)}{x(0.5x+0.5y-0.5z)^{\frac{1}{2}} \times 67.082},$$

so that

$$26.403 = \frac{6-x}{x(0.5x+0.5y-0.5z)} \dots\dots\dots \text{I (a)}$$

$$6.422 = \frac{(3-u-y)x}{(6-x)(y+0.5u)} \dots\dots\dots \text{II (a)}$$

$$211.4 = \frac{66.827(3-u-y)}{u(y+0.5u)^{\frac{1}{2}} \times 67.082},$$

so that

$$212.21 = \frac{3-u-y}{u(y+0.5u)^{\frac{1}{2}}} \dots\dots\dots \text{III (a)}$$

$$0.059759 = \frac{z}{(28.214-0.5z)^{\frac{1}{2}}(0.5x+0.5y-0.5z)^{\frac{1}{2}}} \dots\dots\dots \text{IV (a)}$$

By trial and error it is found that $u=0.0685$ and equation III (a) then gives $y=0.00625$. Equation II (a) then gives $x=0.48992$ and equation I (a) gives $z=0.13327$. Inserting these values in the right-hand side of equation IV (a) gives 0.05897 as against 0.05976 on the left-hand side. The composition of the products of combustion at 4500° F. abs. is as shown in the following table which has been drawn up for the purpose of calculating the entropy of the mixture at this condition.

Gas	m	S_T	mS_T	$\frac{\Sigma m}{m}$	$\log_{10} \frac{\Sigma m}{m}$	$4.575m \log_{10} \frac{\Sigma m}{m}$
CO ₂	5.51008	77.230	425.543	6.8050	0.83283	20.994
CO	0.48992	63.866	31.289	76.536	1.88386	4.222
H ₂ O	2.92525	66.127	193.438	12.818	1.10782	14.826
H ₂	0.04050	46.891	1.899	925.84	2.96654	0.550
OH	0.06850	59.803	4.097	547.39	2.73830	0.858
O ₂	0.18146	60.278	12.027	208.64	2.31522	1.022
NO	0.13327	67.248	8.962	281.36	2.44926	1.493
N ₂	28.14737	62.186	1750.372	1.3321	0.12454	16.038

$$Em \approx \underline{37.49635}; \quad E(mS_T) = \underline{2427.627}; \quad E\left(4.575m \log_{10} \frac{\Sigma m}{m}\right) = \underline{60.903}$$

The pressure at this state point is given by the expression

$$\begin{aligned} P_{4500} &= \frac{4500 \times 37.49635 P_2}{m_2 T_2} \\ &= \frac{4500 \times 37.49635 \times 8.8083}{37.214 \times 1057} \\ &= 37.784 \text{ atmospheres.} \end{aligned}$$

The entropy at this point is therefore

$$\begin{aligned} S_{4500} &= 2427.627 + 60.903 - 37.49635 \times 4.575 \times 1.57732 \\ &= 2217.947 \text{ E.U.} \end{aligned}$$

Repeating the calculation in the same way with $T=4000^\circ \text{ F. abs.}$ gives $P=33.422$ atmospheres and $S=2171.604$ E.U.

In order that the constant volume curve may be drawn on the T/S field it is necessary to calculate the entropies for a series of temperatures ranging from 1057° F. abs. (the temperature at the end of compression) to 3500° F. abs. Up to this temperature it may be assumed that the degree of dissociation is negligible. At 1500° F. abs. the entropy is found tabularly as follows :

Gas	m	S_T	mS_T
CO ₂	6.000	62.048	372.288
H ₂ O	3.000	53.831	161.643
N ₂	28.214	53.130	1499.010
$\Sigma m = \underline{37.214};$		$\Sigma(mS_T) = \underline{2032.941}$	

$$\begin{aligned} P_{1500} &= \frac{8.8083 \times 1500}{1057} \\ &= 12.5 \text{ atmospheres.} \end{aligned}$$

$$\begin{aligned} S_{1500} &= 2032.941 + 52.283 - 186.753 \\ &= 1898.471 \text{ E.U.} \end{aligned}$$

The entropies at a series of progressively increasing temperatures are calculated in the same way and tabulated below.

$T = 1500$	2000	2500	3000	3500
$S = 1898.47$	1970.86	2030.68	2081.68	2126.11

Dealing now with the constant cooling curve 4-1, the entropy at the temperature level T is given by the expression

$$\Sigma m S_T - \Sigma m 4.575 \log_{10} \frac{P_{1000}}{P_{600}} + \Sigma m 4.575 \log_{10} \frac{\Sigma m}{m},$$

and with $T = 1000^\circ \text{F. abs.}$

$$\begin{aligned} \Sigma m S_T &= 6.000 \times 57.284 + 3.000 \times 50.257 + 28.214 \times 50.158 \\ &= 1909.633 \text{ E.U.} \end{aligned}$$

also, from S_{600} as given on p. 62

$$\Sigma m 4.575 \log_{10} \frac{\Sigma m}{m} = 52.283 \text{ E.U.}$$

The value of P_{1000} is $1000/600 = 1.6667$ atmospheres, so that

$$\begin{aligned} \Sigma m 4.575 \log_{10} 1.6667/1 \\ &= 37.214 \times 4.575 \times 0.22186 \\ &= 37.771 \text{ E.U.} \end{aligned}$$

We therefore have

$$\begin{aligned} S_{1000} &= 1909.633 + 52.283 - 37.771 \\ &= 1924.145 \text{ E.U.} \end{aligned}$$

The table below gives the values of the entropies at various temperature levels up to $3000^\circ \text{F. abs.}$, obtained by adding

$$\Sigma m \frac{R}{J} \log_e 5 = 37.214 \times 4.575 \times 0.69897 = 119.002 \text{ E.U.}$$

to the corresponding entropy values in the table above for the curve 2-3.

$T^\circ \text{F. abs.}$	S
600	1817.048
1000	1924.145
1500	2017.473
2000	2089.864
2500	2149.683
3000	2200.683

At temperatures above $3000^\circ \text{F. abs.}$ the dissociation effects may no longer be neglected so that the method already explained for determining the true composition of the dissociated products has again to be adopted. The equilibrium constants are as follows :

$$K_{x_{\text{CO}_2}} = \frac{6-x}{x(0.5x+0.5y-0.5z)^{\frac{1}{2}}} \left(\frac{m_1 T_1}{P_1 T_4} \right)^{\frac{1}{2}} \dots \dots \dots \text{I (b)}$$

$$K_{p_{w.g.}} = \frac{(3-u-y)x}{(6-x)(y+0.5u)} \dots\dots\dots \text{II (b)}$$

$$K_{p_{OH}} = \frac{3-u-y}{u(y+0.5u)^{\frac{1}{2}}} \left(\frac{m_1 T_1}{P_1 T_4} \right)^{\frac{1}{2}} \dots\dots\dots \text{III (b)}$$

$$K_{p_{NO}} = \frac{z}{(28.214 - 0.5z)^{\frac{1}{2}} (0.5x + 0.5y - 0.5z)^{\frac{1}{2}}} \dots\dots\dots \text{IV (b)}$$

Substituting for m_1 , T_1 and P_1 gives

$$K_{p_{CO_2}} = \frac{149.43(6-x)}{x(0.5x + 0.5y - 0.5z)^{\frac{1}{2}}} \cdot \frac{1}{T_4^{\frac{1}{2}}} \dots\dots\dots \text{I (c)}$$

$$K_{p_{w.g.}} = \frac{(3-u-y)x}{(6-x)(y+0.5u)} \dots\dots\dots \text{II (c)}$$

$$K_{p_{OH}} = \frac{149.43(3-u-y)}{u(y+0.5u)^{\frac{1}{2}} \times T_4^{\frac{1}{2}}} \dots\dots\dots \text{III (c)}$$

$$K_{p_{NO}} = \frac{z}{(28.214 - 0.5z)^{\frac{1}{2}} (0.5x + 0.5y - 0.5z)^{\frac{1}{2}}} \dots\dots\dots \text{IV (c)}$$

At $T_4 = 3500^\circ \text{ F. abs.}$ the above equations become

$$1180.3 = \frac{149.43(6-x)}{x(0.5x + 0.5y - 0.5z)^{\frac{1}{2}} \times 59.161}$$

which gives

$$467.29 = \frac{6-x}{x(0.5x + 0.5y - 0.5z)^{\frac{1}{2}}} \dots\dots\dots \text{I (d)}$$

$$4.549 = \frac{(3-u-y)x}{(6-x)(y+0.5u)} \dots\dots\dots \text{II (d)}$$

$$11390 = \frac{149.43(3-u-y)}{u(y+0.5u)^{\frac{1}{2}} \times 59.161},$$

which gives

$$4509 = \frac{3-u-y}{u(y+0.5u)^{\frac{1}{2}}} \dots\dots\dots \text{III (d)}$$

$$0.017282 = \frac{z}{(28.214 - 0.5z)^{\frac{1}{2}} (0.5x + 0.5y - 0.5z)^{\frac{1}{2}}} \dots\dots\dots \text{IV (d)}$$

Solving these four equations in the way already explained gives the following values :

$$x = 0.072560$$

$$y = 0.004350$$

$$z = 0.015789$$

$$u = 0.007390$$

from which $P_{3500} = 5.8400$ atmospheres.

$$S_{3500} = 2248.355 \text{ E.U.}$$

It will be found that at $T_4 = 3930^\circ \text{ F. abs.}$ the entropy of the products

is the same as that at the beginning of expansion and at this temperature the following values are obtained :

$$x = 0.241830$$

$$y = 0.008400$$

$$z = 0.052969$$

$$u = 0.029100$$

from which $P_{3930} = 6.5746$ atmospheres,

$$S_{3930} = 2288.765 \text{ E.U.}$$

Thermal Efficiency

The heat supplied under the conditions stated above, i.e. when dissociation is taken into account, is given by the area under the curve 2-3, while the heat rejected is given by the area under the curve 4-1.

Area under curve 2-3 is H_{r_2}

$$= 1362140 \text{ B.Th.U.}$$

Area under curve 4-1

$$= 907918 \text{ B.Th.U.}$$

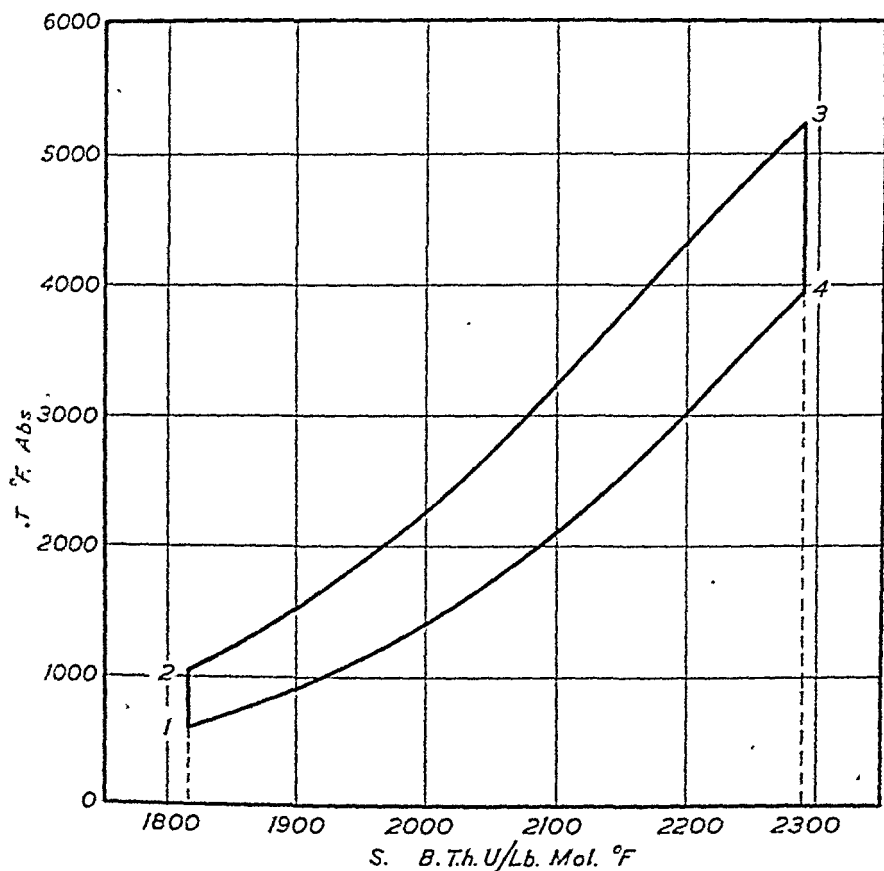


FIG. 19.

Hence the ideal efficiency is

$$\begin{aligned} &= \frac{1362140 - 967918}{1362140} \\ &= 0.3335 \text{ or } 33.35\%. \end{aligned}$$

It is not possible in this case to determine accurately the ideal efficiency of this cycle when no dissociation occurs as the maximum temperature is then above 5400° F. abs., which is the upper limit of temperature for which properties of H₂O are available.

BIBLIOGRAPHY

- (1) Heck, R. C. H., 'The New Specific Heats', *Mechanical Engineering*, vol. 62 (1940), p. 9 and vol. 63 (1941), p. 126.
- (2) Geyer, E. W., 'The New Specific Heats and Energy Charts for Gases', *Engineering*, vol. 159 (1945), p. 381 and p. 423.
- (3) Goodenough, G. A. and Felbeck, G. T., 'An Investigation of the Maximum Temperatures and Pressures attainable in the Combustion of Gaseous and Liquid Fuels'. University of Illinois, *Bulletin No. 139*, Engineering Experiment Station (March, 1924).
- (4) Sainte-Claire Deville, 'Leçons sur la Dissociation', *Leçons de Chimie* (1864-65), Hachette et Cie (Paris, 1866).
- (5) Gibbs, J. W., *The Scientific Papers of J. W. Gibbs* (New York, 1906).
- (6) Horstmann, *Ber. deut. chem. Ges.*, I, 137 (1869); *Ann. Chem. Pharm.*, 170, 192 (1873).
- (7) Haber, *Thermodynamik der technischen Gasreaktionen*, Oldenbourg (München, 1905). English translation by Lamb; Longmans, Green and Co. (1908).
- (8) Nernst, *Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes*, Halle (1918).
- (9) Van't Hoff, *Z. physik. Chem.* I, 481 (1857).
- (10) Clerk, D., *The Gas, Petrol and Oil Engine*, Longmans, Green and Co. (London, 1909).
- (11) Tizard, H. T. and Pye, D. R., 'The Character of Various Fuels for Internal Combustion Engines', *Automobile Engineer*, Feb. 1921, p. 55; March 1921, p. 98; April 1921, p. 131.
- (12) See (3).
- (13) Schüle, W., *Technische Thermodynamik*, Springer (Berlin, 1923).
- (14) See (7).
- (15) Debye, *Annalen der Physik* (1912).
- (16) Johnston, H. L. and Walker, M. K., 'Heat Capacity, Entropy and Free Energy of Gaseous Oxygen from Near Zero Absolute to 5000° K', *J.A.C.S.*, vol. 55 (1933), p. 172.
- (17) Pitzer, K., 'Chemical Equilibria, Free Energies and Heat Contents for Gaseous Hydrocarbons', *Chemical Reviews*, vol. 27 (1940), p. 39.
- (18) Parks, G. S., 'Some Free Energy Data for Typical Hydrocarbons containing Six or More Carbon Atoms', *Chemical Reviews*, vol. 27 (1940), p. 75.
- (19) Matthews, J. H., 'The accurate Measurement of Heats of Vaporization of Liquids', *J.A.C.S.*, vol. 48 (1926), p. 562.

TABLES

SYMBOLS USED IN TABLES

- E Internal Energy, B.Th.U./lb. mol.
- $-\frac{F}{T}$ Function of Free Energy, B.Th.U./lb. mol ° F.
- H Total Heat, B.Th.U./lb. mol.
- H_v Lower Heat of Reaction at Constant Volume, B.Th.U./lb. mol.
- H_p Lower Heat of Reaction at Constant Pressure, B.Th.U./lb. mol.
- K_p Equilibrium Constant.
- S Entropy, B.Th.U./lb. mol ° F.
- ΔL_0 Heat of Reaction at Absolute Zero Temperature.
- $\frac{R}{J} = 1.9869$ B.Th.U./lb. mol ° F.

REFERENCE TO PROPERTIES

The properties incorporated in the tables are based on the following authorities. A useful summary of work in this field is given by Lewis, B. and von Elbe, G., *J.A.C.S.*, vol. 57 (1935), p. 612.

CO and N₂. Johnston, H. L. and Davis, C. O., *J.A.C.S.*, vol. 56 (1934), p. 271.

NO. Johnston, H. L. and Chapman, A. T., *J.A.C.S.*, vol. 55 (1933), p. 153.

O₂. Johnston, H. L. and Walker, M. K., *J.A.C.S.*, vol. 55 (1933), p. 172.

O₃ (High Temperatures). Johnston, H. L. and Walker, M. K., *J.A.C.S.*, vol. 57 (1935), p. 682.

CO₂. Kassel, L. S., *J.A.C.S.*, vol. 56 (1934), p. 1835.

H₂O. Gordon, A. R., *J. Ch. Physics*, vol. 2 (1934), p. 65 and p. 614.

H₂O (Corrections). Wilson, E. B., *J. Ch. P.*, vol. 4 (1936), p. 526.

H₂O (Corrections). Stephenson, C. C. and McMahon, H. O., *J. Ch. P.*, vol. 7 (1939), p. 614.

H₂. Davis, C. O. and Johnston, H. L., *J.A.C.S.*, vol. 56 (1934), p. 1045.

OH. Dwyer, R. J. and Oldenbourg, O., *J. Ch. P.*, vol. 12 (1944), p. 351.

CH₄, C₂H₂, C₂H₄, and C₃H₁₈. Pitzer, K. *Chemical Reviews*, vol. 27 (1940), p. 39 *et seq.*

THERMAL PROPERTIES OF GASES OXYGEN

$T^{\circ}\text{F.}$ Abs.	S	E	H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
100					100
200					200
300					300
400	46.996 1.527	1985 489	2780 687	40.045 1.545	400
500	48.523 1.293	2474 502	3467 711	41.690 1.281	500
600	49.816 1.097	2976 515	4168 713	42.871 1.070	600
700	50.913 0.965	3491 525	4881 724	43.941 0.930	700
800	51.878 0.866	4016 537	5605 736	44.871 0.827	800
900	52.744 0.789	4553 551	6341 750	45.698 0.744	900
1000	53.533 0.727	5104 565	7091 764	46.442 0.677	1000
1100	54.260 0.675	5669 578	7855 776	47.119 0.623	1100
1200	54.935 0.630	6247 589	8631 788	47.742 0.578	1200
1300	55.565 0.592	6836 600	9419 799	48.320 0.539	1300
1400	56.157 0.557	7436 609	10218 807	48.859 0.505	1400
1500	56.714 0.526	8045 618	11025 817	49.364 0.475	1500
1600	57.240 0.499	8663 625	11842 824	49.839 0.450	1600
1700	57.739 0.475	9288 632	12666 830	50.289 0.427	1700
1800	58.214 0.453	9920 639	13496 838	50.716 0.407	1800
1900	58.667 0.433	10559 645	14334 844	51.123 0.388	1900
2000	59.100 0.413	11204 650	15178 848	51.511 0.370	2000
2100	59.513 0.397	11854 653	16026 852	51.881 0.358	2100
2200	59.910 0.380	12507 657	16878 856	52.239 0.340	2200
2300	60.290 0.367	13164 662	17734 860	52.579 0.331	2300
2400	60.657 0.352	13826 665	18594 864	52.910 0.316	2400
2500	61.009 0.341	14491 669	19458 868	53.226 0.307	2500
2600	61.350 0.329	15160 673	20326 872	53.533 0.295	2600
2700	61.679 0.319	15833 678	21198 876	53.828 0.286	2700
2800	61.998 0.308	16511 680	22074 879	54.114 0.277	2800
2900	62.306 0.299	17191 684	22953 883	54.391 0.268	2900
3000	62.605 0.291	17875 687	23836 885	54.659 0.262	3000
3100	62.896 0.282	18562 690	24721 889	54.921 0.254	3100
3200	63.178 0.275	19252 693	25610 892	55.175 0.247	3200
3300	63.453 0.267	19945 697	26502 895	55.422 0.240	3300
3400	63.720 0.260	20642 700	27397 899	55.662 0.233	3400
3500	63.980 0.254	21342 703	28296 902	55.895 0.228	3500
3600	64.234 0.249	22045 707	29198 905	56.123 0.224	3600
3700	64.483 0.242	22752 710	30103 909	56.347 0.217	3700
3800	64.725 0.236	23462 711	31012 910	56.564 0.212	3800
3900	64.961 0.231	24173 714	31922 913	56.776 0.207	3900
4000	65.192 0.227	24887 718	32835 916	56.983 0.203	4000
4100	65.419 0.221	25605 720	33751 919	57.186 0.200	4100
4200	65.640 0.217	26325 723	34670 922	57.386 0.194	4200
4300	65.857 0.213	27048 726	35592 924	57.580 0.190	4300
4400	66.070 0.208	27774 727	36516 926	57.770 0.187	4400
4500	66.278 0.204	28501 731	37442 930	57.957 0.183	4500

OXYGEN (continued)

$T^{\circ}\text{F.}$ Abs.	S	E	H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
4600	66-482 0.201	29232 735	38372 933	58-140 0.181	4600
4700	66-683 0.197	29967 738	39305 937	58-321 0.174	4700
4800	66-880 0.194	30705 740	40242 939	58-495 0.174	4800
4900	67-074 0.190	31445 743	41181 942	58-669 0.170	4900
5000	67-264 0.187	32188 746	42123 943	58-839 0.168	5000
5100	67-451 0.183	32933 747	43066 946	59-007 0.164	5100
5200	67-634 0.181	33680 749	44012 948	59-171 0.161	5200
5300	67-815 0.178	34429 750	44960 948	59-332 0.161	5300
5400	67-993 0.175	35179 753	45908 952	59-493 0.156	5400
5500	68-168 0.172	35932 756	46860 955	59-649 0.152	5500
5600	68-340 0.170	36688 760	47815 958	59-801 0.151	5600
5700	68-510 0.167	37488 762	48773 961	59-952 0.149	5700
5800	68-677 0.165	38210 765	49734 964	60-101 0.147	5800
5900	68-842 0.162	38975 769	50698 967	60-248 0.145	5900
6000	69-004 0.160	39744 771	51665 970	60-393 0.142	6000
6100	69-164 0.158	40515 773	52635 972	60-535 0.141	6100
6200	69-322 0.156	41288 777	53607 975	60-676 0.138	6200
6300	69-478 0.154	42065 777	54582 976	60-814 0.137	6300
6400	69-632 0.151	42848 778	55558 977	60-951 0.136	6400
6500	69-783 0.149	43620 779	56535 978	61-087 0.133	6500
6600	69-932 0.147	44399 782	57513 980	61-220 0.130	6600
6700	70-079 0.145	45181 782	58493 981	61-350 0.129	6700
6800	70-224 0.144	45963 784	59474 983	61-479 0.128	6800
6900	70-368 0.141	46747 786	60457 984	61-607 0.126	6900
7000	70-509 0.140	47533 786	61441 985	61-733 0.125	7000
7100	70-649 0.138	48319 788	62426 987	61-858 0.122	7100
7200	70-787 0.137	49107 791	63413 989	61-980 0.122	7200
7300	70-924 0.135	49898 791	64402 990	62-102 0.121	7300
7400	71-059 0.133	50689 793	65392 992	62-223 0.118	7400
7500	71-192 0.132	51482 796	66384 994	62-341 0.117	7500
7600	71-324 0.130	52278 797	67378 996	62-458 0.116	7600
7700	71-454 0.128	53075 799	68374 998	62-574 0.115	7700
7800	71-582 0.127	53874 800	69372 999	62-689 0.114	7800
7900	71-709 0.126	54674 802	70371 1000	62-803 0.112	7900
8000	71-835 0.124	55476 802	71371 1001	62-915 0.111	8000
8100	71-959 0.123	56278 804	72372 1003	63-026 0.109	8100
8200	72-082 0.121	57082 805	73375 1003	63-135 0.108	8200
8300	72-203 0.120	57887 806	74378 1005	63-243 0.107	8300
8400	72-323 0.119	58693 806	75383 1005	63-350 0.106	8400
8500	72-442 0.118	59499 808	76388 1006	63-456 0.105	8500
8600	72-560 0.116	60307 809	77394 1008	63-561 0.104	8600
8700	72-676 0.115	61116 810	78402 1008	63-665 0.103	8700
8800	72-791 0.114	61926 810	79411 1009	63-768 0.101	8800
8900	72-905 0.113	62736 811	80420 1009	63-869 0.101	8900
9000	73-018	63547	81429	63-970	9000

NITROGEN (*continued*)

$T^{\circ}\text{F.}$ Abs.	S	E	H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
4600	62 378 0 189	27471 679	36611 577	54-419 0 173	4600
4700	62-567 0-185	28150 680	37488 879	54-592 0-166	4700
4800	62-752 0-182	28830 681	38367 880	54-758 0-162	4800
4900	62 934 0 178	29511 682	39247 881	54-924 0-162	4900
5000	63 112 0 175	30193 683	40128 881	55-086 0-160	5000
5100	63 287 0 171	30876 684	41009 883	55-246 0-157	5100
5200	63 458 0 169	31560 685	41892 884	55-403 0-153	5200
5300	63-627 0-165	32245 686	42776 885	55-556 0-152	5300
5400	63-792 0-163	32931 687	43661 885	55-708 0-148	5400
5500	63-955 0-160	33618 688	44546 887	55-856 0-146	5500
5600	64-115 0-157	34306 689	45433 888	56-002 0-144	5600
5700	64-272 0-154	34995 690	46321 888	56-146 0-140	5700
5800	64-426 0-152	35685 690	47209 889	56-286 0-139	5800
5900	64-578 0-150	36375 692	48098 890	56-425 0-138	5900
6000	64-728 0-147	37067 692	48988 891	56-563 0-135	6000
6100	64-875 0-145	37759 693	49879 892	56-698 0-133	6100
6200	65-020 0-143	38452 695	50771 893	56 831 0-131	6200
6300	65-163 0-141	39147 695	51664 894	56-962 0-130	6300
6400	65-304 0-139	39842 696	52558 895	57-092 0-129	6400
6500	65-443 0-137	40538 697	53453 896	57-221 0-126	6500
6600	65-580 0-135	41235 697	54349 896	57-347 0-124	6600
6700	65-715 0-133	41932 698	55245 896	57-471 0-121	6700
6800	65-848 0-130	42630 698	56141 897	57-592 0-121	6800
6900	65-978 0-129	43328 700	57038 898	57-713 0-119	6900
7000	66-107 0-127	44028 700	57936 899	57-832 0-117	7000
7100	66-234 0-126	44728 700	58835 899	57-949 0-116	7100
7200	66-360 0-124	45428 702	59734 900	58-065 0-115	7200
7300	66-484 0-123	46130 702	60634 901	58-180 0-114	7300
7400	66-607 0-122	46832 703	61535 902	58-294 0-111	7400
7500	66-729 0-120	47535 704	62437 902	58-405 0-110	7500
7600	66-849 0-118	48239 704	63339 903	58-515 0-110	7600
7700	66-967 0-117	48943 704	64242 903	58-625 0-109	7700
7800	67-084 0-115	49647 704	65145 903	58-734 0-107	7800
7900	67-199 0-114	50351 704	66048 903	58-841 0-106	7900
8000	67-313 0-112	51055 704	66951 903	58-947 0-103	8000
8100	67-425 0-110	51759 705	67854 903	59 050 0-102	8100
8200	67-535 0-108	52464 705	68757 903	59-152 0-100	8200
8300	67-643 0-107	53169 705	69660 904	59-252 0-100	8300
8400	67-750 0-106	53874 705	70564 904	59-352 0-099	8400
8500	67-856 0-105	54579 706	71468 904	59-451 0-098	8500
8600	67-961 0-105	55285 706	72372 905	59-549 0-097	8600
8700	68-066 0-104	55991 707	73277 906	59-646 0-096	8700
8800	68-170 0-102	56698 708	74183 906	59-742 0-093	8800
8900	68-272 0-101	57406 708	75089 907	59-835 0-093	8900
9000	68-373	58114	75996	59-928	9000

CARBON DIOXIDE

$T^{\circ}\text{F.}$ Abs.	S		E		H		$-\frac{I}{T}$	$T^{\circ}\text{F.}$ Abs.	
100								100	
200								200	
300								300	
400	48.620	1.853	2100	636	2895	834	41.383	1.633	400
500	50.473	1.631	2736	698	3729	897	43.016	1.378	500
600	52.104	1.465	3434	751	4626	949	44.394	1.211	600
700	53.569	1.337	4185	803	5575	1002	45.605	1.080	700
800	54.906	1.233	4988	847	6577	1046	46.685	0.983	800
900	56.139	1.145	5835	887	7623	1086	47.668	0.907	900
1000	57.284	1.068	6722	916	8709	1115	48.575	0.846	1000
1100	58.352	1.004	7638	959	9824	1157	49.421	0.784	1100
1200	59.356	0.946	8597	982	10981	1181	50.205	0.742	1200
1300	60.302	0.896	9579	1009	12162	1208	50.947	0.701	1300
1400	61.198	0.850	10588	1033	13370	1231	51.648	0.666	1400
1500	62.048	0.810	11621	1055	14601	1254	52.314	0.635	1500
1600	62.858	0.773	12676	1074	15855	1273	52.949	0.607	1600
1700	63.631	0.739	13750	1093	17128	1291	53.556	0.582	1700
1800	64.370	0.708	14843	1110	18419	1309	54.138	0.557	1800
1900	65.078	0.678	15953	1125	19728	1324	54.695	0.535	1900
2000	65.756	0.652	17078	1138	21052	1336	55.230	0.517	2000
2100	66.408	0.627	18216	1149	22388	1348	55.747	0.499	2100
2200	67.035	0.604	19365	1160	23736	1359	56.246	0.482	2200
2300	67.639	0.582	20525	1170	25095	1368	56.728	0.467	2300
2400	68.221	0.563	21695	1181	26463	1380	57.195	0.452	2400
2500	68.784	0.545	22876	1189	27843	1388	57.647	0.440	2500
2600	69.329	0.527	24065	1197	29231	1396	58.087	0.425	2600
2700	69.856	0.510	25262	1205	30627	1403	58.512	0.414	2700
2800	70.366	0.495	26467	1213	32030	1412	58.926	0.404	2800
2900	70.861	0.481	27680	1219	33442	1418	59.330	0.391	2900
3000	71.342	0.467	28899	1224	34860	1422	59.721	0.384	3000
3100	71.809	0.454	30123	1230	36282	1429	60.105	0.373	3100
3200	72.263	0.441	31353	1235	37711	1434	60.478	0.364	3200
3300	72.704	0.430	32588	1242	39145	1440	60.842	0.355	3300
3400	73.134	0.419	33830	1246	40585	1445	61.197	0.347	3400
3500	73.553	0.408	35076	1248	42030	1447	61.544	0.341	3500
3600	73.961	0.397	36324	1254	43477	1452	61.885	0.330	3600
3700	74.358	0.389	37578	1260	44929	1459	62.215	0.325	3700
3800	74.747	0.379	38838	1263	46388	1462	62.540	0.317	3800
3900	75.126	0.370	40101	1266	47850	1465	62.857	0.310	3900
4000	75.496	0.362	41367	1270	49315	1468	63.167	0.304	4000
4100	75.858	0.355	42637	1274	50783	1473	63.471	0.301	4100
4200	76.213	0.346	43911	1276	52256	1475	63.772	0.292	4200
4300	76.559	0.339	45187	1278	53731	1476	64.064	0.286	4300
4400	76.898	0.332	46465	1281	55207	1480	64.350	0.282	4400
4500	77.230	0.325	47746	1283	56687	1482	64.632	0.277	4500

CARBON DIOXIDE (*continued*)

$T^{\circ}\text{F.}$ Abs.	S	E	H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
4600	77.555 0.319	49029 1286	58169 1484	64.909 0.274	4600
4700	77.874 0.313	50315 1291	59653 1490	65.183 0.265	4700
4800	78.187 0.307	51606 1294	61143 1493	65.448 0.263	4800
4900	78.494 0.300	52900 1297	62636 1496	65.711 0.257	4900
5000	78.794 0.297	54197 1299	64132 1497	65.968 0.255	5000
5100	79.091 0.291	55496 1300	65629 1499	66.223 0.250	5100
5200	79.382 0.285	56796 1301	67128 1500	66.473 0.245	5200
5300	79.667 0.280	58097 1303	68628 1501	66.718 0.244	5300
5400	79.947 0.275	59400 1303	70129 1501	66.962 0.238	5400
5500	80.222 0.271	60703 1304	71630 1503	67.200 0.233	5500
5600	80.493 0.266	62007 1306	73133 1505	67.433 0.232	5600
5700	80.759 0.262	63313 1308	74638 1507	67.665 0.226	5700
5800	81.021 0.258	64621 1310	76145 1509	67.891 0.226	5800
5900	81.279 0.254	65931 1313	77654 1511	68.117 0.222	5900
6000	81.533 0.250	67244 1314	79165 1513	68.339 0.217	6000
6100	81.783 0.246	68558 1316	80678 1515	68.556 0.216	6100
6200	82.029 0.243	69874 1319	82193 1517	68.772 0.213	6200
6300	82.272	71193	83710	68.985	6300

WATER VAPOUR

$T^{\circ}\text{F.}$ Abs.	S	E	H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
100					100
200					200
300					300
400	42.799 1.779	2405 602	3200 798	34.800 1.778	400
500	44.578 1.456	3007 608	3998 800	36.578 1.459	500
600	46.034 1.251	3615 615	4798 813	38.037 1.233	600
700	47.285 1.097	4230 624	5611 823	39.270 1.070	700
800	48.382 0.981	5854 635	6434 834	40.340 0.947	800
900	49.363 0.894	5489 641	7268 849	41.287 0.853	900
1000	50.257 0.824	6130 677	8117 865	42.140 0.776	1000
1100	51.081 0.766	6807 682	8982 881	42.916 0.712	1100
1200	51.847 0.717	7489 697	9863 896	43.628 0.660	1200
1300	52.564 0.676	8186 715	10759 913	44.288 0.615	1300
1400	53.240 0.641	8901 731	11672 929	44.903 0.578	1400
1500	53.881 0.610	9632 747	12601 946	45.481 0.543	1500
1600	54.491 0.583	10379 764	13547 963	46.024 0.515	1600
1700	55.074 0.561	11143 782	14510 980	46.539 0.490	1700
1800	55.635 0.539	11925 799	15490 997	47.029 0.468	1800
1900	56.174 0.521	12724 816	16487 1015	47.497 0.447	1900
2000	56.695 0.503	13540 835	17502 1033	47.944 0.428	2000
2100	57.198 0.488	14375 850	18535 1050	48.372 0.412	2100
2200	57.686 0.473	15225 866	19585 1063	48.784 0.397	2200
2300	58.159 0.460	16091 880	20648 1079	49.181 0.385	2300
2400	58.619 0.446	16971 896	21727 1094	49.566 0.371	2400
2500	59.065 0.434	17867 908	22821 1107	49.937 0.360	2500
2600	59.499 0.423	18775 923	23928 1122	50.297 0.347	2600
2700	59.922 0.412	19698 934	25050 1132	50.644 0.339	2700
2800	60.334 0.403	20632 951	26182 1149	50.983 0.330	2800
2900	60.737 0.392	21583 960	27331 1159	51.313 0.319	2900
3000	61.129 0.384	22543 972	28490 1170	51.632 0.313	3000
3100	61.513 0.376	23515 984	29660 1183	51.945 0.306	3100
3200	61.889 0.368	24499 994	30843 1193	52.251 0.298	3200
3300	62.257 0.359	25493 1007	32036 1205	52.549 0.291	3300
3400	62.616 0.352	26500 1016	33241 1214	52.840 0.283	3400
3500	62.968 0.345	27516 1026	34455 1225	53.123 0.279	3500
3600	63.313 0.337	28542 1033	35680 1232	53.402 0.272	3600
3700	63.650 0.331	29575 1044	36912 1242	53.674 0.267	3700
3800	63.981 0.325	30619 1051	38154 1249	53.941 0.262	3800
3900	64.306 0.318	31670 1057	39403 1256	54.203 0.256	3900
4000	64.624 0.312	32727 1065	40659 1263	54.459 0.252	4000
4100	64.936 0.306	33792 1070	41922 1269	54.711 0.249	4100
4200	65.242 0.300	34862 1078	43191 1276	54.960 0.241	4200
4300	65.542 0.294	35940 1083	44467 1282	55.201 0.237	4300
4400	65.836 0.291	37023 1090	45749 1289	55.438 0.235	4400
4500	66.127 0.284	38113 1097	47038 1295	55.673 0.230	4500

WATER VAPOUR (*continued*)

$T^{\circ}\text{F.}$ Abs.	S	E	H	$-\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
4600	66.411 0.280	39210 1103	48333 1302	55.903 0.228	4600
4700	66.691 0.275	40313 1110	49635 1308	56.131 0.221	4700
4800	66.966 0.271	41423 1114	50943 1313	56.352 0.220	4800
4900	67.237 0.266	42537 1119	52256 1317	56.572 0.216	4900
5000	67.503 0.262	43656 1124	53573 1322	56.788 0.214	5000
5100	67.765 0.258	44780 1127	54895 1326	57.002 0.210	5100
5200	68.023 0.253	45907 1131	56221 1330	57.212 0.206	5200
5300	68.276 0.249	47038 1136	57551 1334	57.418 0.204	5300
5400	68.525	48174	58885	57.622	5400
5500					5500
5600					5600
5700					5700
5800					5800
5900					5900
6000					6000

CARBON MONOXIDE

$T^{\circ}\text{F.}$ Abs.	S	E	H	$-\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
100					100
200					200
300					300
400	45.290 1.544	1985 497	2780 695	38.340 1.544	400
500	46.834 1.269	2482 499	3475 698	39.884 1.265	500
600	48.103 1.079	2981 501	4173 699	41.149 1.073	600
700	49.182 0.936	3482 504	4872 703	42.222 0.927	700
800	50.118 0.830	3986 507	5575 706	43.149 0.819	800
900	50.948 0.753	4493 517	6281 716	43.968 0.736	900
1000	51.701 0.691	5010 527	6997 726	44.704 0.667	1000
1100	52.392 0.639	5537 537	7723 735	45.371 0.611	1100
1200	53.031 0.596	6074 546	8458 745	45.982 0.566	1200
1300	53.627 0.559	6620 556	9203 755	46.548 0.525	1300
1400	54.186 0.526	7176 565	9958 763	47.073 0.492	1400
1500	54.712 0.499	7741 574	10721 773	47.565 0.463	1500
1600	55.211 0.473	8315 582	11494 781	48.028 0.436	1600
1700	55.684 0.451	8897 591	12275 789	48.464 0.414	1700
1800	56.135 0.431	9488 599	13064 798	48.878 0.392	1800
1900	56.566 0.412	10087 605	13862 804	49.270 0.375	1900
2000	56.978 0.396	10692 612	14666 810	49.645 0.359	2000
2100	57.374 0.379	11304 618	15476 817	50.004 0.344	2100
2200	57.753 0.366	11922 624	16293 823	50.348 0.329	2200
2300	58.119 0.352	12546 629	17116 827	50.677 0.318	2300
2400	58.471 0.340	13175 635	17943 834	50.995 0.305	2400
2500	58.811 0.328	13810 638	18777 837	51.300 0.296	2500
2600	59.139 0.317	14448 642	19614 841	51.596 0.284	2600
2700	59.456 0.307	15090 645	20455 843	51.880 0.276	2700
2800	59.763 0.297	15735 649	21298 848	52.156 0.268	2800
2900	60.060 0.288	16384 653	22146 852	52.424 0.258	2900
3000	60.348 0.280	17037 656	22998 854	52.682 0.252	3000
3100	60.628 0.273	17693 658	23852 857	52.934 0.245	3100
3200	60.901 0.264	18351 660	24709 859	53.179 0.238	3200
3300	61.165 0.257	19011 662	25568 860	53.417 0.233	3300
3400	61.422 0.250	19673 665	26428 864	53.650 0.223	3400
3500	61.672 0.244	20338 668	27292 867	53.873 0.222	3500
3600	61.916 0.238	21006 669	28159 867	54.095 0.214	3600
3700	62.154 0.231	21675 671	29026 870	54.309 0.209	3700
3800	62.385 0.227	22346 673	29896 872	54.518 0.205	3800
3900	62.612 0.221	23019 674	30768 873	54.723 0.200	3900
4000	62.833 0.216	23693 676	31641 874	54.923 0.195	4000
4100	63.049 0.210	24369 677	32515 876	55.118 0.192	4100
4200	63.259 0.207	25046 679	33391 878	55.310 0.187	4200
4300	63.466 0.202	25725 680	34269 878	55.497 0.182	4300
4400	63.668 0.198	26405 682	35147 881	55.679 0.180	4400
4500	63.866 0.194	27087 684	36028 882	55.859 0.177	4500

THERMAL PROPERTIES OF GASES
CARBON MONOXIDE (continued)

81

$T^{\circ}\text{F.}$ Abs.	S	E	H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
4600	64-060 0.189	27771 684	36910 883	56-036 0.173	4600
4700	64-249 0.186	28455 685	37793 884	56-209 0.167	4700
4800	64-435 0.183	29140 687	38677 886	56-376 0.167	4800
4900	64-618 0.179	29827 687	39563 886	56-543 0.164	4900
5000	64-797 0.176	30514 688	40449 886	56-707 0.161	5000
5100	64-973 0.172	31202 689	41335 887	56-868 0.158	5100
5200	65-145 0.169	31891 690	42222 889	57-026 0.154	5200
5300	65-314 0.166	32581 690	43111 889	57-180 0.153	5300
5400	65-480 0.163	33271 691	44000 890	57-333 0.149	5400
5500	65-643 0.160	33962 691	44890 890	57-482 0.146	5500
5600	65-803 0.158	34653 692	45780 891	57-628 0.145	5600
5700	65-961 0.155	35345 693	46671 891	57-773 0.142	5700
5800	66-116 0.153	36038 693	47562 892	57-915 0.141	5800
5900	66-269 0.150	36731 694	48454 892	58-056 0.139	5900
6000	66-419 0.148	37425 695	49346 894	58-195 0.136	6000
6100	66-567 0.146	38120 696	50240 895	58-331 0.134	6100
6200	66-713 0.143	38816 698	51135 896	58-465 0.132	6200
6300	66-856 0.141	39514 698	52031 897	58-597 0.130	6300
6400	66-997 0.139	40212 699	52928 898	58-727 0.130	6400
6500	67-136 0.137	40911 699	53826 898	58-857 0.126	6500
6600	67-273 0.135	41610 700	54724 899	58-983 0.125	6600
6700	67-408 0.133	42310 701	55623 899	59-108 0.123	6700
6800	67-541 0.132	43011 701	56522 899	59-231 0.121	6800
6900	67-673 0.130	43712 702	57421 900	59-352 0.121	6900
7000	67-803 0.128	44414 702	58321 901	59-473 0.119	7000
7100	67-931 0.126	45116 702	59222 901	59-592 0.115	7100
7200	68-057 0.124	45818 702	60123 901	59-707 0.115	7200
7300	68-181 0.123	46520 702	61024 901	59-822 0.114	7300
7400	68-304 0.121	47222 702	61925 901	59-936 0.112	7400
7500	68-425 0.119	47924 703	62826 902	60-048 0.112	7500
7600	68-544 0.118	48627 704	63728 902	60-160 0.110	7600
7700	68-662 0.117	49331 704	64630 903	60-270 0.109	7700
7800	68-779 0.115	50035 704	65533 903	60-379 0.108	7800
7900	68-894 0.114	50739 706	66436 904	60-487 0.105	7900
8000	69-008 0.112	51445 706	67340 905	60-592 0.104	8000
8100	69-120 0.111	52151 707	68245 906	60-696 0.104	8100
8200	69-231 0.110	52858 709	69151 907	60-800 0.102	8200
8300	69-341 0.109	53567 709	70058 908	60-902 0.101	8300
8400	69-450 0.108	54276 710	70966 909	61-003 0.101	8400
8500	69-558 0.106	54986 711	71875 909	61-104 0.100	8500
8600	69-664 0.105	55697 711	72784 910	61-204 0.097	8600
8700	69-769 0.104	56408 711	73694 910	61-301 0.096	8700
8800	69-873 0.103	57119 712	74604 910	61-397 0.094	8800
8900	69-976 0.101	57831 713	75514 910	61-491 0.094	8900
9000	70-077	58544	76424	61-585	9000

HYDROGEN

$T^{\circ}\text{F.}$ Abs.	S	E	H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
100					100
200					200
300					300
400	20.249 1.504	1916 479	2711 677	22.473 1.505	400
500	30.753 1.256	2395 492	3388 691	23.978 1.233	500
600	32.009 1.069	2887 496	4079 694	25.211 1.050	600
700	33.078 0.928	3383 498	4773 697	26.261 0.908	700
800	34.006 0.822	3881 500	5470 699	27.169 0.804	800
900	34.828 0.736	4381 501	6169 700	27.973 0.722	900
1000	35.564 0.668	4882 502	6869 701	28.695 0.655	1000
1100	36.232 0.610	5384 504	7570 702	29.350 0.598	1100
1200	36.842 0.564	5888 506	8272 705	29.948 0.553	1200
1300	37.406 0.523	6394 508	8977 707	30.501 0.511	1300
1400	37.929 0.489	6902 510	9684 708	31.012 0.478	1400
1500	38.418 0.458	7412 513	10392 712	31.490 0.446	1500
1600	38.876 0.434	7925 516	11104 715	31.936 0.422	1600
1700	39.310 0.411	8441 521	11819 719	32.358 0.398	1700
1800	39.721 0.392	8962 526	12538 725	32.756 0.377	1800
1900	40.113 0.375	9488 532	13263 731	33.133 0.358	1900
2000	40.488 0.359	10020 538	13994 736	33.491 0.342	2000
2100	40.847 0.344	10558 542	14730 741	33.833 0.326	2100
2200	41.191 0.331	11100 547	15471 746	34.159 0.312	2200
2300	41.522 0.319	11647 550	16217 748	34.471 0.301	2300
2400	41.841 0.309	12197 556	16965 755	34.772 0.290	2400
2500	42.150 0.299	12753 564	17720 763	35.062 0.278	2500
2600	42.449 0.290	13317 570	18483 769	35.340 0.268	2600
2700	42.739 0.282	13887 577	19252 778	35.608 0.259	2700
2800	43.021 0.274	14464 582	20030 778	35.867 0.253	2800
2900	43.295 0.267	15046 587	20808 786	36.120 0.244	2900
3000	43.562 0.259	15633 592	21594 790	36.364 0.236	3000
3100	43.821 0.253	16225 598	22384 797	36.600 0.230	3100
3200	44.074 0.247	16823 603	23181 802	36.830 0.223	3200
3300	44.321 0.240	17426 607	23983 805	37.053 0.218	3300
3400	44.561 0.235	18033 612	24788 811	37.271 0.210	3400
3500	44.796 0.230	18645 618	25599 817	37.481 0.208	3500
3600	45.026 0.225	19263 622	26416 820	37.689 0.201	3600
3700	45.251 0.220	19885 627	27236 826	37.890 0.197	3700
3800	45.471 0.216	20512 631	28062 830	38.087 0.192	3800
3900	45.687 0.211	21143 635	28892 834	38.279 0.188	3900
4000	45.898 0.206	21778 638	29726 836	38.467 0.182	4000
4100	46.104 0.203	22416 642	30562 841	38.649 0.182	4100
4200	46.307 0.198	23058 646	31403 845	38.831 0.175	4200
4300	46.505 0.195	23704 649	32248 847	39.006 0.172	4300
4400	46.700 0.191	24353 653	33095 852	39.178 0.169	4400
4500	46.891 0.188	25006 656	33947 855	39.347 0.166	4500

THERMAL PROPERTIES OF GASES

HYDROGEN (*continued*)

83

$T^{\circ}\text{F.}$ Abs.	S	E	H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
4600	47-070 0-185	25662 660	34802 858	39-513 0-165	4600
4700	47-264 0-181	26322 663	35660 862	39-678 0-158	4700
4800	47-445 0-179	26985 666	36522 865	39-836 0-158	4800
4900	47-624 0-175	27651 668	37387 867	39-994 0-154	4900
5000	47-799 0-172	28319 672	38254 870	40-148 0-152	5000
5100	47-971 0-170	28991 674	39124 873	40-300 0-150	5100
5200	48-141 0-166	29665 677	39997 876	40-450 0-145	5200
5300	48-307 0-164	30342 679	40873 877	40-595 0-146	5300
5400	48-471 0-161	31021 680	41750 879	40-741 0-141	5400
5500	48-632 0-159	31701 682	42629 881	40-882 0-140	5500
5600	48-791 0-156	32383 685	43510 883	41-022 0-137	5600
5700	48-947 0-153	33068 688	44393 887	41-159 0-135	5700
5800	49-100 0-152	33756 691	45280 890	41-291 0-134	5800
5900	49-252 0-151	34447 694	46170 892	41-428 0-132	5900
6000	49-403 0-148	35141 695	47062 894	41-560 0-129	6000
6100	49-551 0-147	35836 697	47956 896	41-689 0-128	6100
6200	49-698 0-143	36533 701	48852 899	41-817 0-127	6200
6300	49-841 0-141	37234 702	49751 901	41-944 0-125	6300
6400	49-982 0-140	37936 703	50652 902	42-069 0-123	6400
6500	50-122 0-138	38639 705	51554 904	42-192 0-122	6500
6600	50-260 0-137	39344 708	52458 906	42-314 0-120	6600
6700	50-397 0-136	40052 709	53364 908	42-434 0-119	6700
6800	50-533 0-134	40761 711	54272 910	42-553 0-117	6800
6900	50-667 0-131	41472 714	55182 912	42-670 0-115	6900
7000	50-798 0-129	42186 715	56094 914	42-785 0-113	7000
7100	50-927 0-127	42901 717	57008 916	42-898 0-111	7100
7200	51-054 0-126	43618 719	57924 917	43-009 0-110	7200
7300	51-180 0-125	44337 719	58841 918	43-119 0-110	7300
7400	51-305 0-123	45056 721	59759 920	43-229 0-108	7400
7500	51-428 0-121	45777 723	60679 921	43-337 0-107	7500
7600	51-549 0-121	46500 724	61600 923	43-444 0-106	7600
7700	51-670 0-120	47224 725	62523 924	43-550 0-105	7700
7800	51-790 0-118	47949 726	63447 925	43-655 0-104	7800
7900	51-908 0-117	48675 728	64372 926	43-759 0-103	7900
8000	52-025 0-115	49403 729	65298 928	43-862 0-102	8000
8100	52-140 0-114	50132 730	66226 929	43-964 0-101	8100
8200	52-254 0-113	50862 732	67155 930	44-065 0-100	8200
8300	52-367 0-112	51594 732	68085 931	44-165 0-098	8300
8400	52-479 0-110	52326 734	69016 933	44-263 0-097	8400
8500	52-589 0-109	53060 737	69949 935	44-360 0-096	8500
8600	52-698 0-108	53797 737	70884 936	44-456 0-095	8600
8700	52-806 0-107	54534 739	71820 938	44-551 0-094	8700
8800	52-913 0-106	55273 741	72758 939	44-645 0-094	8800
8900	53-019 0-106	56014 741	73697 940	44-739 0-093	8900
9000	53-125	56755	74637	44-832	9000

HYDROXYL (OH)

$T^{\circ}\text{F.}$ Abs.	S	E	H	$-\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
100					100
200					200
300					300
400					400
500					500
600	44.711 1.097	3060 506	4252 704	37.625 1.103	600
700	45.808 0.933	3506 505	4956 704	38.728 0.938	700
800	46.741 0.828	4071 503	5660 702	39.666 0.834	800
900	47.569 0.745	4574 509	6362 708	40.500 0.744	900
1000	48.314 0.676	5083 509	7070 708	41.244 0.675	1000
1100	48.990 0.613	5592 510	7778 708	41.919 0.612	1100
1200	49.603 0.574	6102 511	8486 710	42.531 0.572	1200
1300	50.177 0.527	6613 511	9196 710	43.103 0.525	1300
1400	50.704 0.485	7124 515	9906 713	43.628 0.482	1400
1500	51.189 0.461	7639 516	10619 715	44.110 0.456	1500
1600	51.650 0.439	8155 525	11334 724	44.566 0.430	1600
1700	52.089 0.419	8680 535	12058 733	44.996 0.406	1700
1800	52.508 0.402	9215 544	12791 743	45.402 0.385	1800
1900	52.910 0.382	9759 547	13534 746	45.787 0.365	1900
2000	53.292 0.366	10306 552	14280 750	46.152 0.349	2000
2100	53.658 0.352	10858 556	15030 755	46.501 0.334	2100
2200	54.010 0.339	11414 562	15785 761	46.835 0.320	2200
2300	54.349 0.323	11976 567	16546 765	47.155 0.304	2300
2400	54.672 0.313	12543 573	17311 772	47.459 0.293	2400
2500	54.985 0.305	13116 576	18083 775	47.752 0.285	2500
2600	55.290 0.296	13692 583	18858 782	48.037 0.275	2600
2700	55.586 0.286	14275 591	19640 789	48.312 0.264	2700
2800	55.872 0.282	14866 597	20429 796	48.576 0.259	2800
2900	56.154 0.272	15463 602	21225 801	48.835 0.249	2900
3000	56.426 0.263	16065 611	22026 809	49.084 0.239	3000
3100	56.689 0.256	16676 614	22835 813	49.323 0.232	3100
3200	56.945 0.251	17290 619	23648 818	49.555 0.227	3200
3300	57.196 0.248	17909 622	24466 820	49.782 0.225	3300
3400	57.444 0.239	18531 625	25286 824	50.007 0.216	3400
3500	57.683 0.232	19156 630	26110 829	50.223 0.209	3500
3600	57.915 0.230	19786 632	26939 830	50.432 0.208	3600
3700	58.145 0.225	20418 635	27769 834	50.640 0.203	3700
3800	58.370 0.218	21053 639	28603 838	50.843 0.196	3800
3900	58.588 0.211	21692 643	29441 842	51.039 0.189	3900
4000	58.799 0.208	22335 648	30283 846	51.228 0.186	4000
4100	59.007 0.204	22983 652	31129 851	51.414 0.182	4100
4200	59.211 0.202	23635 658	31980 857	51.596 0.180	4200
4300	59.413 0.198	24293 663	32837 861	51.776 0.176	4300
4400	59.611 0.192	24956 663	33698 862	51.952 0.171	4400
4500	59.803 0.189	25619 665	34560 864	52.123 0.168	4500

THERMAL PROPERTIES OF GASES

HYDROXYL (continued)

85

$T^{\circ}\text{F.}$ Abs.	S	E	H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
4600	59-092 0-188	26284 671	35424 869	52-291 0-167	4600
4700	60-180 0-185	26955 674	36293 873	52-458 0-164	4700
4800	60-365 0-182	27629 675	37166 874	52-622 0-161	4800
4900	60-547 0-177	28304 676	38040 875	52-783 0-157	4900
5000	60-724 0-173	28980 678	38915 876	52-940 0-154	5000
5100	60-897 0-169	29658 678	39791 877	53-094 0-151	5100
5200	61-066 0-167	30336 678	40668 877	53-245 0-149	5200
5300	61-233 0-163	31014 678	41545 877	53-394 0-146	5300
5400	61-396 0-162	31692 679	42422 877	53-540 0-145	5400
5500	61-558 0-158	32371 680	43299 879	53-685 0-142	5500
5600	61-716 0-156	33051 683	44178 881	53-827 0-140	5600
5700	61-872 0-154	33734 684	45059 883	53-967 0-138	5700
5800	62-026 0-152	34418 687	45942 886	54-105 0-136	5800
5900	62-178 0-149	35105 692	46828 890	54-241 0-133	5900
6000	62-327 0-148	35797 694	47718 893	54-374 0-132	6000
6100	62-475 0-146	36491 697	48611 896	54-506 0-130	6100
6200	62-621 0-142	37188 701	49507 899	54-636 0-126	6200
6300	62-763 0-141	37889 704	50406 903	54-762 0-125	6300
6400	62-904 0-140	38593 707	51309 906	54-887 0-124	6400
6500	64-044 0-139	39300 709	52215 908	55-011 0-123	6500
6600	63-183 0-138	40009 715	53123 913	55-134 0-122	6600
6700	63-321 0-137	40724 716	54036 915	55-256 0-121	6700
6800	63-458 0-136	41440 719	54951 918	55-377 0-120	6800
6900	63-594 0-134	42159 724	55869 922	55-497 0-118	6900
7000	63-728 0-132	42883 726	56791 925	55-615 0-116	7000
7100	63-860 0-129	43609 729	57716 928	55-731 0-113	7100
7200	63-989 0-128	44338 731	58644 929	55-844 0-112	7200
7300	64-117 0-127	45069 731	59573 930	55-956 0-111	7300
7400	64-244 0-125	45800 732	60503 931	56-067 0-109	7400
7500	64-369 0-124	46532 733	61434 932	56-176 0-108	7500
7600	64-493 0-122	47265 734	62366 932	56-284 0-107	7600
7700	64-615 0-121	47999 735	63298 934	56-391 0-106	7700
7800	64-736 0-119	48734 735	64232 934	56-497 0-105	7800
7900	64-855 0-118	49469 736	65166 934	56-602 0-104	7900
8000	64-973 0-117	50205 736	66100 935	56-706 0-103	8000
8100	65-090 0-115	50941 737	67035 936	56-809 0-102	8100
8200	65-205 0-113	51678 738	67971 936	56-911 0-101	8200
8300	65-318 0-112	52416 738	68907 937	57-012 0-100	8300
8400	65-430 0-111	53154 739	69844 938	57-112 0-099	8400
8500	65-541 0-110	53893 740	70782 939	57-211 0-098	8500
8600	65-651 0-108	54633 741	71721 939	57-309 0-096	8600
8700	65-759 0-106	55374 741	72660 940	57-405 0-095	8700
8800	65-865 0-105	56115 743	73600 941	57-500 0-094	8800
8900	65-970 0-104	56858 743	74541 942	57-594 0-093	8900
9000	66-074	57601	75483	57-687	9000

NITRIC OXIDE (NO)

$T^{\circ}\text{F.}$ Abs.	S		E		H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
100							100
200							200
300							300
400							400
500							500
600	51.142	1.110	3213	516	4405 714	43.801 1.138	600
700	52.252	0.954	3729	520	5119 719	44.939 0.969	700
800	53.206	0.856	4249	527	5838 726	45.908 0.861	800
900	54.062	0.773	4776	535	6564 734	46.769 0.768	900
1000	54.835	0.710	5311	542	7298 741	47.537 0.700	1000
1100	55.545	0.650	5853	549	8039 747	48.237 0.636	1100
1200	56.195	0.598	6402	560	8786 759	48.873 0.578	1200
1300	56.793	0.581	6962	571	9545 770	49.451 0.555	1300
1400	57.374	0.543	7533	587	10315 785	50.006 0.511	1400
1500	57.917	0.516	8120	600	11100 799	50.517 0.479	1500
1600	58.433	0.488	8720	610	11899 809	50.996 0.450	1600
1700	58.921	0.471	9330	619	12708 817	51.446 0.432	1700
1800	59.392	0.441	9949	621	13525 820	51.878 0.406	1800
1900	59.833	0.422	10570	629	14345 828	52.284 0.389	1900
2000	60.255	0.397	11199	638	15173 836	52.673 0.369	2000
2100	60.652	0.393	11837	642	16009 841	53.042 0.358	2100
2200	61.045	0.381	12479	647	16850 846	53.400 0.339	2200
2300	61.426	0.366	13126	653	17696 851	53.739 0.327	2300
2400	61.792	0.348	13779	654	18547 853	54.066 0.314	2400
2500	62.140	0.333	14433	655	19400 854	54.380 0.304	2500
2600	62.473	0.324	15088	656	20254 855	54.684 0.295	2600
2700	62.797	0.308	15744	657	21109 856	54.979 0.284	2700
2800	63.105	0.299	16401	658	21965 856	55.263 0.274	2800
2900	63.404	0.288	17059	658	22821 857	55.537 0.267	2900
3000	63.692	0.282	17717	661	23678 859	55.804 0.259	3000
3100	63.974	0.273	18378	662	24537 861	56.063 0.252	3100
3200	64.247	0.264	19040	664	25398 863	56.315 0.245	3200
3300	64.511	0.259	19704	669	26261 867	56.560 0.237	3300
3400	64.770	0.256	20373	671	27128 870	56.797 0.231	3400
3500	65.026	0.249	21044	675	27998 874	57.028 0.227	3500
3600	65.275	0.241	21719	679	28872 877	57.255 0.221	3600
3700	65.516	0.236	22398	680	29749 879	57.476 0.214	3700
3800	65.752	0.231	23078	683	30628 882	57.690 0.211	3800
3900	65.983	0.223	23761	685	31510 884	57.901 0.205	3900
4000	66.206	0.219	24446	688	32394 886	58.106 0.200	4000
4100	66.425	0.213	25134	689	33280 888	58.306 0.195	4100
4200	66.638	0.207	25823	689	34168 888	58.501 0.191	4200
4300	66.845	0.204	26512	690	35056 888	58.692 0.188	4300
4400	67.049	0.199	27202	690	35944 889	58.880 0.183	4400
4500	67.248	0.195	27892	690	36833 889	59.063 0.181	4500

THERMAL PROPERTIES OF GASES NITRIC OXIDE (continued)

87

$T^{\circ}\text{F.}$ Abs.	S	E	H	$\frac{F}{T}$	$T^{\circ}\text{F.}$ Abs.
4600	67-443 0-191	28582 692	37722 890	59-244 0-176	4600
4700	67-634 0-188	29274 692	38612 891	59-420 0-173	4700
4800	67-822 0-183	29966 692	39503 891	59-593 0-170	4800
4900	68-005 0-181	30658 693	40394 892	59-763 0-167	4900
5000	68-186 0-177	31351 696	41286 894	59-930 0-163	5000
5100	68-363 0-174	32047 697	42180 896	60-093 0-160	5100
5200	68-537 0-171	32744 699	43076 898	60-253 0-158	5200
5300	68-708 0-169	33443 702	43974 900	60-411 0-156	5300
5400	68-877 0-164	34145 702	44874 901	60-567 0-153	5400
5500	69-041 0-163	34847 702	45775 901	60-720 0-151	5500
5600	69-204 0-161	35549 702	46676 901	60-871 0-148	5600
5700	69-365 0-157	36251 702	47577 901	61-019 0-145	5700
5800	69-522 0-153	36953 702	48478 901	61-164 0-143	5800
5900	69-675 0-152	37655 702	49379 901	61-307 0-141	5900
6000	69-827 0-149	38357 702	50280 901	61-448 0-139	6000
6100	69-976 0-147	39059 703	51181 901	61-587 0-137	6100
6200	70-123 0-147	39762 703	52082 901	61-724 0-136	6200
6300	70-270 0-146	40465 703	52983 901	61-860 0-136	6300
6400	70-416 0-141	41168 704	53884 903	61-996 0-131	6400
6500	70-557 0-137	41872 706	54787 905	62-127 0-127	6500
6600	70-691 0-135	42578 708	55692 906	62-254 0-125	6600
6700	70-829 0-133	43286 708	56598 907	62-379 0-124	6700
6800	70-962 0-132	43994 709	57505 908	62-503 0-123	6800
6900	71-091 0-130	44703 711	58413 909	62-626 0-122	6900
7000	71-224 0-130	45414 712	59322 911	62-748 0-120	7000
7100	71-354 0-127	46126 713	60233 912	62-868 0-118	7100
7200	71-481 0-124	46839 715	61145 913	62-986 0-117	7200
7300	71-605 0-124	47554 715	62058 914	63-103 0-115	7300
7400	71-729 0-122	48269 717	62972 916	63-218 0-114	7400
7500	71-851 0-122	48986 718	63888 916	63-332 0-113	7500
7600	71-973 0-119	49704 719	64804 918	63-445 0-111	7600
7700	72-092 0-118	50423 720	65722 919	63-556 0-110	7700
7800	72-210 0-116	51143 720	66641 919	63-666 0-108	7800
7900	72-326 0-115	51863 722	67560 920	63-774 0-107	7900
8000	72-441 0-114	52585 722	68480 921	63-881 0-106	8000
8100	72-555 0-113	53307 723	69401 922	63-987 0-105	8100
8200	72-668 0-111	54030 724	70323 922	64-092 0-103	8200
8300	72-779 0-110	54754 724	71245 923	64-195 0-102	8300
8400	72-889 0-109	55478 725	72168 924	64-297 0-101	8400
8500	72-998 0-108	56203 728	73092 926	64-398 0-100	8500
8600	73-106 0-106	56931 728	74018 927	64-498 0-099	8600
8700	73-212 0-105	57659 730	74945 929	64-597 0-098	8700
8800	73-317 0-105	58389 735	75874 933	64-695 0-097	8800
8900	73-422 0-104	59124 736	76807 935	64-792 0-096	8900
9000	73-526	59860	77742	64-888	9000

THERMAL PROPERTIES OF GASES
EQUILIBRIUM CONSTANTS

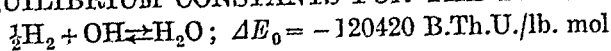
T° F. Abs.	$K_p = \frac{p_{\text{CO}_2}}{p_{\text{CO}} \cdot p_{\text{O}_2}^{\frac{1}{2}}}$		$K_p = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} \cdot p_{\text{O}_2}^{\frac{1}{2}}}$		$K_p = \frac{p_{\text{H}_2\text{O}} \cdot p_{\text{CO}}}{p_{\text{H}_2} \cdot p_{\text{CO}_2}}$		T° F. Abs.
	CO + $\frac{1}{2}\text{O}_2 = \text{CO}_2$		$\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$		$\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$		
	Log ₁₀ K _p	K _p	Log ₁₀ K _p	K _p	Log ₁₀ K _p	K _p	
600	39.80	6.3096 × 10 ³⁹	35.840	6.918 × 10 ³⁵	-4.231	5.875 × 10 ⁻⁵	600
700	33.46	2.8840 × 10 ³³	30.141	1.384 × 10 ³⁰	-3.318	4.808 × 10 ⁻⁴	700
800	28.70	5.0119 × 10 ²⁸	25.972	9.370 × 10 ²⁵	-2.638	2.301 × 10 ⁻³	800
900	25.00	1 × 10 ²⁵	22.882	7.621 × 10 ²²	-2.115	7.674 × 10 ⁻³	900
1000	22.04	1.0965 × 10 ²²	20.333	2.153 × 10 ²⁰	-1.703	1.982 × 10 ⁻²	1000
1100	19.61	4.0738 × 10 ¹⁹	18.242	1.746 × 10 ¹⁸	-1.370	4.266 × 10 ⁻²	1100
1200	17.59	3.8905 × 10 ¹⁷	16.497	3.141 × 10 ¹⁶	-1.096	8.017 × 10 ⁻²	1200
1300	15.89	7.7625 × 10 ¹⁵	15.017	1.040 × 10 ¹⁵	-0.8673	0.1357	1300
1400	14.42	2.6303 × 10 ¹⁴	13.747	5.585 × 10 ¹³	-0.6745	0.2116	1400
1500	13.15	1.4125 × 10 ¹³	12.643	4.395 × 10 ¹²	-0.5099	0.3091	1500
1600	12.04	1.0965 × 10 ¹²	11.676	4.742 × 10 ¹¹	-0.3683	0.4283	1600
1700	11.07	1.1740 × 10 ¹¹	10.821	6.622 × 10 ¹⁰	-0.2459	0.5677	1700
1800	10.20	1.5849 × 10 ¹⁰	10.061	1.151 × 10 ¹⁰	-0.1384	0.7271	1800
1900	9.423	2.6485 × 10 ⁹	9.379	2.393 × 10 ⁹	-0.0435	0.9047	1900
2000	8.724	5.2066 × 10 ⁸	8.765	5.821 × 10 ⁸	0.0407	1.098	2000
2100	8.093	1.2388 × 10 ⁸	8.208	1.614 × 10 ⁸	0.1154	1.304	2100
2200	7.519	3.3037 × 10 ⁷	7.701	5.023 × 10 ⁷	0.1825	1.522	2200
2300	6.996	9.9083 × 10 ⁶	7.238	1.730 × 10 ⁷	0.2426	1.748	2300
2400	6.517	3.2885 × 10 ⁶	6.814	6.516 × 10 ⁶	0.2971	1.982	2400
2500	6.077	1.1940 × 10 ⁶	6.422	2.642 × 10 ⁶	0.3460	2.218	2500
2600	5.670	4.6774 × 10 ⁵	6.061	1.151 × 10 ⁶	0.3908	2.459	2600
2700	5.295	1.9724 × 10 ⁶	5.726	5.321 × 10 ⁵	0.4313	2.700	2700
2800	4.946	8.8308 × 10 ⁴	5.415	2.600 × 10 ⁵	0.4689	2.944	2800
2900	4.622	4.1879 × 10 ⁴	5.125	1.333 × 10 ⁵	0.5027	3.182	2900
3000	4.320	2.0893 × 10 ⁴	4.854	7.145 × 10 ⁴	0.5336	3.417	3000

THERMAL PROPERTIES OF GASES
EQUILIBRIUM CONSTANTS (*continued*)

89

T° F. Abs.	$K_p = \frac{P_{CO_2}}{P_{CO} \cdot P_{O_2}^{\frac{1}{2}}}$		$K_p = \frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}}$		$K_p = \frac{P_{H_2O} \cdot P_{CO}}{P_{H_2} \cdot P_{CO_2}}$		T° F. Abs.
	CO + $\frac{1}{2}$ O ₂ = CO ₂		H ₂ + $\frac{1}{2}$ O ₂ = H ₂ O		CO ₂ + H ₂ = CO + H ₂ O		
	Log ₁₀ K _p	K _p	Log ₁₀ K _p	K _p	Log ₁₀ K _p	K _p	
3100	4.037	1.0889 × 10 ⁴	4.600	3.981 × 10 ⁴	0.5624	3.651	3100
3200	3.773	5.9293 × 10 ³	4.363	2.307 × 10 ⁴	0.5893	3.884	3200
3300	3.525	3.3497 × 10 ³	4.139	1.377 × 10 ⁴	0.6140	4.112	3300
3400	3.291	1.9543 × 10 ³	3.929	8492	0.6372	4.337	3400
3500	3.072	1.1803 × 10 ³	3.730	5370	0.6579	4.549	3500
3600	2.865	732.82	3.543	3491	0.6776	4.760	3600
3700	2.668	465.59	3.365	2317	0.6962	4.968	3700
3800	2.483	304.09	3.197	1574	0.7132	5.167	3800
3900	2.307	202.77	3.037	1089	0.7296	5.365	3900
4000	2.141	138.36	2.885	767.4	0.7447	5.555	4000
4100	1.982	95.040	2.741	550.8	0.7593	5.745	4100
4200	1.832	67.920	2.604	401.8	0.7722	5.918	4200
4300	1.688	48.753	2.473	297.2	0.7847	6.091	4300
4400	1.551	35.563	2.345	221.3	0.7963	6.256	4400
4500	1.420	26.303	2.228	169.0	0.8077	6.422	4500
4600	1.295	19.724	2.113	129.7	0.8179	6.575	4600
4700	1.176	14.997	2.004	100.9	0.8273	6.719	4700
4800	1.062	11.535	1.898	79.07	0.8365	6.863	4800
4900	0.9521	8.9557	1.797	62.66	0.8452	7.002	4900
5000	0.8467	7.0259	1.701	50.23	0.8538	7.142	5000
5100	0.7450	5.5705	1.608	40.55	0.8616	7.271	5100
5200	0.6491	4.4576	1.518	32.96	0.8691	7.398	5200
5300	0.5561	3.5983	1.432	27.04	0.8763	7.521	5300
5400	0.4667	2.9289	1.349	22.34	0.8824	7.628	5400

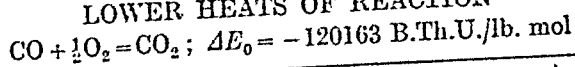
EQUILIBRIUM CONSTANTS FOR THE REACTION



$$K_p = \frac{p_{\text{H}_2\text{O}}}{p_{\text{OH}} \cdot p_{\text{H}_2}^{\frac{1}{2}}}$$

$T^\circ \text{ F.}$ Abs.	$\text{Log}_{10} K_p$	K_p	$T^\circ \text{ F.}$ Abs.	$\text{Log}_{10} K_p$	K_p
600	41.204	1.560×10^{41}	3100	5.0638	1.152×10^5
700	34.851	7.096×10^{34}	3200	4.7895	6.159×10^4
800	30.080	1.202×10^{30}	3300	4.5314	3.400×10^4
900	26.361	2.296×10^{26}	3400	4.2877	1.940×10^4
1000	23.381	2.404×10^{23}	3500	4.0566	1.139×10^4
1100	20.939	8.690×10^{20}	3600	3.8407	6.930×10^3
1200	18.901	7.962×10^{18}	3700	3.6361	4326
1300	17.173	1.489×10^{17}	3800	3.4413	2763
1400	15.691	4.909×10^{15}	3900	3.2571	1808
1500	14.406	2.547×10^{14}	4000	3.0826	1210
1600	13.379	2.393×10^{13}	4100	2.9108	814.3
1700	12.284	1.923×10^{12}	4200	2.7585	573.5
1800	11.399	2.506×10^{11}	4300	2.6070	404.6
1900	10.606	4.037×10^{10}	4400	2.4623	289.9
2000	9.8920	7.798×10^9	4500	2.3250	211.4
2100	9.2454	1.760×10^9	4600	2.1930	156.0
2200	8.6573	4.543×10^8	4700	2.0669	116.7
2300	8.1196	1.317×10^8	4800	1.9451	88.12
2400	7.6276	4.242×10^7	4900	1.8289	67.44
2500	7.1742	1.494×10^7	5000	1.7176	52.19
2600	6.7555	5.695×10^6	5100	1.6109	40.82
2700	6.3668	2.327×10^6	5200	1.5082	32.23
2800	6.0066	1.014×10^6	5300	1.4094	25.67
2900	5.6704	4.682×10^5	5400	1.3140	20.61
3000	5.3563	2.272×10^5			

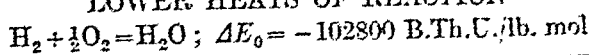
LOWER HEATS OF REACTION



$T^\circ \text{F.}$ Abs.	H_g	H_p	$T^\circ \text{F.}$ Abs.	H_g	H_p
400	121041 105	121438 205	3400	116329 230	119706 130
500	121146 52	121613 151	3500	116099 231	119576 132
600	121198 8	121794 107	3600	115868 232	119444 133
700	121206 37	121901 63	3700	115636 232	119311 133
800	121169 71	121961 28	3800	115404 233	119178 133
900	121098 95	121992 5	3900	115171 234	119045 134
1000	121003 106	121997 7	4000	114937 234	118911 135
1100	120897 133	121990 34	4100	114703 234	118776 135
1200	120764 142	121956 42	4200	114469 235	118641 135
1300	120622 153	121914 51	4300	114234 235	118506 136
1400	120469 163	121860 61	4400	113999 236	118370 137
1500	120306 172	121796 73	4500	113763 236	118233 137
1600	120134 180	121723 80	4600	113527 237	118096 137
1700	119954 186	121643 87	4700	113290 237	117959 138
1800	119768 191	121556 92	4800	113053 237	117821 138
1900	119577 198	121464 98	4900	112816 238	117683 138
2000	119379 201	121366 102	5000	112578 238	117545 139
2100	119178 204	121264 105	5100	112340 239	117406 139
2200	118974 208	121159 108	5200	112101 239	117267 140
2300	118766 210	121051 111	5300	111862 239	117127 139
2400	118556 213	120940 114	5400	111623 237	116988 138
2500	118343 217	120826 117	5500	111390 235	116850 137
2600	118126 218	120709 119	5600	111155 235	116713 136
2700	117908 222	120590 123	5700	110920 235	116577 135
2800	117686 223	120467 123	5800	110685 235	116442 135
2900	117463 224	120344 125	5900	110450 235	116307 134
3000	117239 226	120219 127	6000	110216 234	116173 134
3100	117013 227	120092 127	6100	109982 233	116039 134
3200	116786 228	119965 129	6200	109749 233	115905 134
3300	116558 229	119836 130	6300	109516	115771

THERMAL PROPERTIES OF GASES

LOWER HEATS OF REACTION



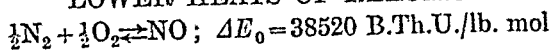
$T^\circ \text{F.}$ Abs.	H_v	H_p	$T^\circ \text{F.}$ Abs.	H_v	H_p
100			3100	104791 41	107871 58
200			3200	104759 44	107929 55
300			3300	104706 52	107985 47
400	103304 121	103702 220	3400	104654 54	108032 45
500	103425 135	103922 234	3500	104600 56	108077 44
600	103560 139	104156 238	3600	104544 58	108121 41
700	103693 136	104394 236	3700	104486 62	108162 37
800	103835 135	104630 235	3800	104424 64	108199 36
900	103970 134	104865 233	3900	104360 65	108235 34
1000	104104 111	105098 210	4000	104295 68	108269 32
1100	104215 108	105308 207	4100	104227 68	108301 31
1200	104323 103	105515 203	4200	104159 71	108332 28
1300	104426 93	105718 192	4300	104088 71	108360 28
1400	104519 84	105910 183	4400	104017 73	108398 27
1500	104603 75	106093 175	4500	103944 75	108415 24
1600	104678 64	106268 163	4600	103869 76	108439 23
1700	104742 55	106431 154	4700	103793 78	108462 22
1800	104797 47	106585 147	4800	103715 78	108484 21
1900	104844 38	106732 137	4900	103637 79	108505 20
2000	104882 28	106869 127	5000	103558 80	108525 20
2100	104910 19	106996 119	5100	103478 80	108545 20
2200	104929 9	107115 108	5200	103398 80	108565 20
2300	104938 1	107223 100	5300	103318 81	108585 16
2400	104939 7	107323 93	5400	103237	108601
2500	104932 10	107416 89	5500		
2600	104922 14	107505 85	5600		
2700	104908 17	107590 83	5700		
2800	104891 31	107673 67	5800		
2900	104860 32	107740 67	5900		
3000	104828 37	107809 62	6000		

LOWER HEATS OF REACTION

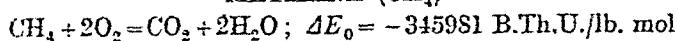
 $\frac{1}{2}\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O}; \Delta E_0 = -120420 \text{ B.Th.U./lb. mol}$

$T^\circ \text{F.}$ Abs.	H_v	H_p	$T^\circ \text{F.}$ Abs.	H_v	H_p
600	121318 139	121904 238	3100	121693 71	124772 29
700	121457 130	122142 229	3200	121622 73	124801 26
800	121587 118	122371 218	3300	121549 82	124827 17
900	121705 109	122589 218	3400	121467 85	124844 15
1000	121814 83	122807 183	3500	121382 87	124859 12
1100	121897 80	122990 180	3600	121295 90	124871 9
1200	121977 67	123170 170	3700	121205 95	124880 5
1300	122044 50	123349 138	3800	121110 96	124885 3
1400	122094 39	123487 136	3900	121014 96	124888 3
1500	122133 25	123623 124	4000	120918 97	124891 3
1600	122158 19	123747 119	4100	120821 97	124894 3
1700	122177 14	123866 113	4200	120724 97	124897 2
1800	122191 8	123970 107	4300	120627 98	124899 1
1900	122199 3	124086 97	4400	120529 100	124900 1
2000	122196 14	124183 85	4500	120429 102	124899 3
2100	122182 23	124268 76	4600	120227 104	124896 4
2200	122159 31	124344 69	4700	120223 105	124892 6
2300	122128 38	124413 61	4800	120118 106	124886 6
2400	122090 45	124474 54	4900	120012 109	124880 10
2500	122045 50	124528 50	5000	119903 110	124870 11
2600	121995 55	124578 46	5100	119793 112	124859 12
2700	121940 56	124624 44	5200	119681 114	124847 15
2800	121884 61	124668 36	5300	119576 119	124832 20
2900	121823 65	124704 34	5400	119448	124812
3000	121758 65	124738 34			

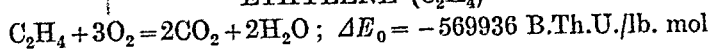
LOWER HEATS OF REACTION



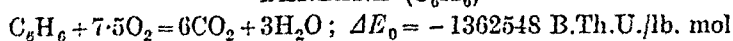
$T^\circ \text{ F.}$ Abs.	$H_v = H_p$	$T^\circ \text{ F.}$ Abs.	$H_v = H_p$	$T^\circ \text{ F.}$ Abs.	$H_v = H_p$
100		3100	38880 6	6100	38440 31
200		3200	38874 6	6200	38409 31
300		3300	38868 7	6300	38378 31
400		3400	38861 7	6400	38347 32
500		3500	38854 7	6500	38315 32
600	38756 3	3600	38847 7	6600	38283 32
700	38759 5	3700	38840 7	6700	38251 32
800	38764 7	3800	38833 8	6800	38219 32
900	38771 9	3900	38825 9	6900	38187 32
1000	38780 0	4000	38816 9	7000	38155 32
1100	38780 2	4100	38807 9	7100	38123 33
1200	38778 4	4200	38798 10	7200	38090 32
1300	38774 2	4300	38788 11	7300	38058 32
1400	38772 5	4400	38777 11	7400	38026 32
1500	38777 7	4500	38766 15	7500	37994 32
1600	38784 9	4600	38751 15	7600	37962 32
1700	38793 10	4700	38736 16	7700	37930 32
1800	38803 11	4800	38720 17	7800	37898 31
1900	38814 12	4900	38703 17	7900	37867 31
2000	38826 13	5000	38686 18	8000	37836 31
2100	38839 14	5100	38668 18	8100	37805 31
2200	38853 12	5200	38650 19	8200	37774 30
2300	38865 11	5300	38631 19	8300	37744 30
2400	38876 9	5400	38612 20	8400	37714 30
2500	38885 5	5500	38592 20	8500	37684 29
2600	38890 3	5600	38572 22	8600	37655 29
2700	38893 2	5700	38550 24	8700	37626 29
2800	38895 3	5800	38526 27	8800	37597 24
2900	38892 6	5900	38499 29	8900	37573 23
3000	38886 6	6000	38470 30	9000	37550

METHANE (CH₄)

$T^\circ \text{F.}$ $Abz.$	S	E	H	$H_2 = H_c$
400	42-153 1-618	2405 512	3200 710	345446 350
500	43-771 1-578	2917 691	3910 890	345096 201
600	45-349 1-477	3608 762	4800 960	344895 190
700	46-826 1-347	4370 811	5760 1010	344705 189
800	48-173 1-247	5181 861	6770 1060	344516 182
900	49-420 1-194	6042 927	7830 1126	344334 158
1000	50-614 1-135	6969 1004	8956 1203	344176 114
1100	51-769 1-118	7973 1077	10159 1275	344062 92
1200	52-887 1-086	9050 1148	11434 1347	343970 50
1300	53-973 1-055	10198 1215	12781 1414	343920 22
1400	55-028 1-030	11413 1284	14195 1482	343898 7
1500	56-058 1-007	12697 1350	15677 1549	343905 37
1600	57-065 0-987	14047 1417	17226 1616	343942 65
1700	58-052 0-968	15464 1480	18842 1678	344007 87
1800	59-020 0-943	16944 1546	20520 1745	344094 118
1900	59-963 0-929	18490 1612	22265 1811	344212 145
2000	60-892 0-915	20102 1678	24076 1876	344357 170
2100	61-807 0-903	21780 1742	25952 1941	344527 197
2200	62-710 0-891	23522 1805	27893 2004	344724 231
2300	63-601 0-879	25327 1868	29897 2066	344955 260
2400	64-480 0-868	27195 1927	31963 2126	345215 286
2500	65-348	29122	34089	345501

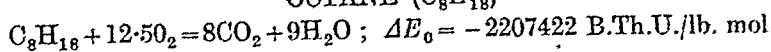
ETHYLENE (C_2H_4)

$T^\circ \text{ F.}$ Abs.	S	E	H	$H_p = H_v$
400	49.236 2.610	2084 1070	2879 1268	568965 61
500	51.846 2.410	3154 1219	4147 1418	569026 131
600	54.256 2.210	4373 1331	5565 1529	569157 144
700	56.466 2.010	5704 1402	7094 1601	569301 123
800	58.476 1.840	7106 1459	8695 1658	569424 106
900	60.316 1.720	8565 1530	10353 1729	569530 109
1000	62.036 1.620	10095 1595	12082 1794	569639 113
1100	63.656 1.530	11690 1655	13876 1853	569752 118
1200	65.186 1.460	13345 1721	15729 1920	569870 130
1300	66.646 1.395	15066 1781	17649 1980	570000 135
1400	68.041 1.345	16847 1849	19629 2047	570135 148
1500	69.386 1.300	18696 1914	21676 2113	570283 164
1600	70.686 1.265	20610 1987	23789 2186	570447 186
1700	71.951 1.230	22597 2053	25975 2251	570633 199
1800	73.181 1.205	24650 2128	28226 2327	570832 229
1900	74.386 1.180	26778 2198	30553 2397	571061 251
2000	75.566 1.155	28976 2262	32950 2460	571312 266
2100	76.721 1.135	31238 2334	35410 2533	571578 293
2200	77.856 1.115	33572 2400	37943 2599	571871 323
2300	78.971 1.095	35972 2469	40542 2667	572194 353
2400	80.066 1.080	38441 2547	43209 2746	572547 390
2500	81.146	40988	45955	572937

BENZENE (C_6H_6)

$T^\circ F.$ Abs.	S^*		E^*		H^*		H_v		H_p	
400	0	3.831	0	1525	0	1724	1363312	428	1362915	527
500	3.831	3.788	1525	1885	1724	2083	1362884	336	1362388	436
600	7.619	3.735	3410	2228	3807	2427	1362548	259	1361952	358
700	11.354	3.675	5638	2557	6234	2756	1362289	196	1361594	295
800	15.029	3.611	8195	2870	8990	3068	1362093	90	1361299	190
900	18.640	3.543	11065	3168	12058	3367	1362003	28	1361109	71
1000	22.183	3.474	14233	3448	15425	3646	1362031	191	1361038	91
1100	25.657	3.403	17681	3715	19071	3914	1362222	248	1361129	149
1200	29.060	3.332	21396	3965	22985	4164	1362470	399	1361278	300
1300	32.392	3.258	25361	4200	27149	4399	1362869	504	1361578	404
1400	35.650	3.185	29561	4418	31548	4617	1363373	596	1361982	497
1500	38.835		33979		36165		1363969		1362479	

* Reckoned from $400^\circ F.$ abs.

OCTANE (C_8H_{18})

$T^\circ F.$ Abc.	S		E		H		H_p		H_v	
400	99.644	7.933	9823	3372	10618	3570	2200830	1714	2203613	1021
500	107.577	8.404	13195	4423	14188	4622	2199116	974	2202592	278
600	115.981	8.576	17618	5376	18810	5574	2198142	422	2202314	271
700	124.557	8.300	22994	6026	24384	6225	2197720	148	2202585	549
800	132.857	7.973	29020	6578	30609	6777	2197572	103	2203134	799
900	140.830	7.826	35598	7229	37386	7428	2197675	474	2203933	1171
1000	148.656	7.418	42827	7582	44814	7781	2198149	626	2205104	1322
1100	156.074	7.341	50409	8235	52595	8433	2198775	948	2206426	1641
1200	163.415	7.034	58644	8585	61028	8784	2199723	1122	2208067	1819
1300	170.449	6.774	67229	8937	69812	9136	2200845	1242	2209886	1938
1400	177.223	6.602	76166	9290	78948	9488	2202087	1367	2211824	2060
1500	183.825	6.355	85456	9640	88436	9839	2203454	1505	2213884	2202
1600	190.180	6.123	95096	9893	98275	10092	2204959	1541	2216086	2237
1700	196.303	5.917	104980	10145	108367	10343	2206500	1570	2218323	2263
1800	202.220	5.633	115134	10196	118710	10395	2208070	1425	2220586	2122
1900	207.853	5.364	125330	10236	129105	10435	2209495	1258	2222708	1954
2000	213.217	5.165	135566	10362	139540	10560	2210753	1175	2224662	1868
2100	218.382	5.129	145928	10801	150100	11000	2211928	1416	2226530	2113
2200	223.511	4.992	156729	11003	161100	11202	2213344	1463	2228643	2159
2300	228.503	4.907	167732	11305	172302	11503	2214807	1598	2230802	2291
2400	233.410	4.832	179037	11608	183805	11807	2216405	1721	2233093	2418
2500	238.242		190645		195612		2218126		2235511	

TABLE OF $\frac{RT}{J}$ WHERE $\frac{R}{J}=1.9869$

$T^{\circ} F. Abs.$	$\frac{RT}{J}$	$T^{\circ} F. Abs.$	$\frac{RT}{J}$	$T^{\circ} F. Abs.$	$\frac{RT}{J}$
100	199	3100	6159	6100	12120
200	397	3200	6358	6200	12319
300	596	3300	6557	6300	12517
400	795	3400	6755	6400	12716
500	993	3500	6954	6500	12915
600	1192	3600	7153	6600	13114
700	1390	3700	7351	6700	13312
800	1589	3800	7550	6800	13511
900	1788	3900	7749	6900	13710
1000	1987	4000	7948	7000	13908
1100	2186	4100	8146	7100	14107
1200	2384	4200	8345	7200	14306
1300	2583	4300	8544	7300	14504
1400	2782	4400	8742	7400	14703
1500	2980	4500	8941	7500	14902
1600	3179	4600	9140	7600	15100
1700	3378	4700	9338	7700	15299
1800	3576	4800	9537	7800	15498
1900	3775	4900	9736	7900	15697
2000	3974	5000	9935	8000	15895
2100	4172	5100	10133	8100	16094
2200	4371	5200	10332	8200	16293
2300	4570	5300	10531	8300	16491
2400	4768	5400	10729	8400	16690
2500	4967	5500	10928	8500	16889
2600	5166	5600	11127	8600	17087
2700	5365	5700	11325	8700	17286
2800	5563	5800	11524	8800	17485
2900	5762	5900	11723	8900	17683
3000	5961	6000	11921	9000	17882

TABLE OF $\frac{R}{J} \log_e x = 1.9869 \times 2.30258 \times \log_{10} x = 4.575 \log_{10} x$

x	$4.575 \log_{10} x$	x	$4.575 \log_{10} x$
1.25	0.4434	8.50	4.2521
1.50	0.8056	8.75	4.3097
1.75	1.1119	9.00	4.3656
2.00	1.3772	9.25	4.4201
2.25	1.6112	9.50	4.4731
2.50	1.8206	9.75	4.5247
2.75	2.0099	10.00	4.5750
3.00	2.1828	10.25	4.6240
3.25	2.3419	10.50	4.6719
3.50	2.4891	10.75	4.7187
3.75	2.6262	11.00	4.7644
4.00	2.7544	11.25	4.8090
4.25	2.8749	11.50	4.8527
4.50	2.9884	11.75	4.8954
4.75	3.0959	12.00	4.9372
5.00	3.1978	12.25	4.9782
5.25	3.2947	12.50	5.0184
5.50	3.3871	12.75	5.0577
5.75	3.4755	13.00	5.0963
6.00	3.5600	13.25	5.1341
6.25	3.6412	13.50	5.1713
6.50	3.7191	13.75	5.2077
6.75	3.7940	14.00	5.2435
7.00	3.8663	15.00	5.3806
7.25	3.9361	16.00	5.5088
7.50	4.0034	17.00	5.6293
7.75	4.0685	18.00	5.7429
8.00	4.1316	19.00	5.8503
8.25	4.1928	20.00	5.9522